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Degumming of Hemp Fibers Using Combined Microwave Energy and Deep Eutectic Solvent

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DEGUMMING OF HEMP FIBERS USING COMBINED MICROWAVE ENERGY AND DEEP EUTECTIC SOLVENT

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Textiles, Apparel, and Merchandising

by
Bulbul Ahmed
B.S., University of Dhaka, 2016
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ABSTRACT

Hemp is considered as one of the sustainable agricultural fiber materials. Degumming or surface modification of hemp bast is needed to produce single fibers for ensuing textile and industrial applications. The traditional degumming process necessitates a high amount of alkali, which causes detrimental environmental pollution. This study offers a new method to degum hemp fibers with reduced use of harmful alkali and precious water resources. In this work, hemp bast fibers were degummed by using combined microwave energy and deep eutectic solvent (DES). The properties of hemp fibers manufactured by this method were investigated and compared with the traditional alkali process. Several analytical techniques were used to characterize and perform a comparative analysis of the degummed fibers. Results revealed that the fiber qualities, including fiber surface morphology and UV shielding performance of DES-treated fibers at 1:20 solid-liquor ratio (UPF value was 183.67) were higher than these from the traditional alkali treated (140.75) and untreated raw hemp fibers (127.47). FT-IR, SEM, NMR, and XRD confirmed that degumming using a Microwave-DES treatment at 1:20 solid-liquor ratio had a higher yield with respect to removal of gummy materials (lignin and hemicellulose, etc.). TGA and DSC also confirmed the higher thermal stability of DES-treated fibers. In addition, cellulose content in the Microwave-DES treated samples was increased to 44.82% - 49.95% which was comparable with the increased cellulose content (49.49%) of alkali treated fibers. All these data indicate the effective, less time-consuming, green, and environmentally sustainable protocol for manufacturing hemp fibers.

CHAPTER 1. INTRODUCTION

1.1. Introduction

Hemp has garnered great interest due to its biodegradability, low-cost, and fast-growing capability under mild and harsh weather conditions throughout the world (Dhondt, 2020). As a natural fiber, hemp has been seen as a potential candidate for a myriad of applications in several sectors such as textile industries, paper industries, bio-refineries, and bio-based/biodegradable composite industries (Ouajai & Shanks, 2005; Wang et al., 2020). The chemical composition of hemp bast consists of cellulose, lignin, hemicellulose, pectin, oil-wax, minerals (Keiller et al., 2021; Liu et al., 2017; Liu et al., 2015; Mirski et al., 2017), and other non-cellulosic components. The presence of those non-cellulosic components leads to difficulties in further textile processing of hemp fibers such as spinning, weaving, dyeing, and other finishing processes (Schumacher et al., 2020). Extraction of hemp fibers from the non-cellulosic components is important to obtain high-quality fibers and/or fiber bundles. Thus, the degumming of hemp fiber from the hemp stem is a crucial step for the effective utilization of hemp bast.

At present, there are many methods of degumming hemp fibers, including chemical (Zhu et al., 2021), mechanical (Liu et al., 2017), thermal (Wang et al., 2020; Gedik & Avinc, 2020), water retting, high energy irradiation, (Stelescu et al., 2020) and other methods of degumming. However, there is a need to develop an environmentally friendly and comparatively cheaper degumming process since the methods mentioned above have many disadvantages concerning biodegradability and cost. Microwave heating has gained a lot of attention as a pretreatment process of biomass, lignocellulosic materials, and natural fibers due to its convenience, low hazards and lower treatment times. Nair et al. (2015) found a good effect using a microwave-assisted degumming, evidenced by the NIR analysis of the degummed hemp fibers. In addition,

Deep Eutectic Solvent (DES) is an alternative ionic liquid that has been considered as a biodegradable solvent (Tan et al., 2020). DES has been employed in the surface treatment of the lignocellulosic materials and natural fibers, including ramie (Yu et al., 2020), kenaf bast (Nie et al., 2020), apocynum bast (Song et al., 2019), and has been found to have a comparable degumming effect to that of traditional degumming methods (Alkali, Silane, Bleaching treatment).

The DES treatment of hemp fiber coupled with microwave energy has been seen as a promising alternative solution to degum the hemp bast to attain high-quality hemp fibers with improved mechanical and thermal properties. In this thesis work, combined microwave energy-DES has been used to investigate the degumming effect and surface modification of hemp fibers by analysis of the surface morphology, physical properties, thermal and mechanical properties, and other characterizations of both degummed and undegummed hemp fibers.

1.2. History and Background of Hemp Fibers

Hemp is an annual plant of the *cannabaceae* family, and the scientific name is referred to as *Cannabis Sativa* (Cattaneo et al., 2021). Around the globe, the plant is known by various names: hemp in the US, Canada, and the UK; hanf in Germany; canapa in Italy; and hennep in the Netherlands (Booth, 2005). The cultivation of hemp started around 10-12 BC, and the use of cannabis fibers and seeds in 6-8 BC (Robinson, 1996). It is hypothesized that the hemp was trailed from South Asia to China and western countries. However, it is known that the cultivation of hemp started in India and China; subsequently, and was disseminated throughout other parts of the world, such as Europe and Africa through the Middle East and Russia. Hemp was brought to North America through Peru and Chile by Spanish explorers (Robinson, 1996).

1.3. Botany of Hemp

Cannabis sativa L. is divided into many subcategories or varieties in which the subspecies of Sativa and Indica are the most important in terms of economic significance.



Figure 1.1. Industrial hemp plant (Owen, 2019)

However, *Cannabis sativa* and *Cannabis indica* are mostly known as industrial hemp and marijuana/medicinal hemp (Chaturvedi & Agrawal, 2021). The chemovars of hemp are classified based on the content of THC (tetrahydrocannabinol) and CBD (cannabidiol) content in the hemp. Generally, industrial hemp contains a very low content of THCA (equal to or less than 1%), and the ratio of THC and CBD is higher than 1%. On the other hand, medicinal hemp (marijuana) is composed of a high content of tetrahydrocannabinol acid (THCA) and low content of CBDA (cannabidiolic acid) (Chaturvedi & Agrawal, 2021). Figure 1.1 represents the industrial hemp plant is ready to harvest.

1.4. Morphology/Anatomy of Hemp

Hemp fibers are bast fibers, i.e., hemp fibers are contained within the stalk of the plant as shown in figure 1. 2. The separation of fibers from the surface xylem in hemp stems can be done by machines or hand.

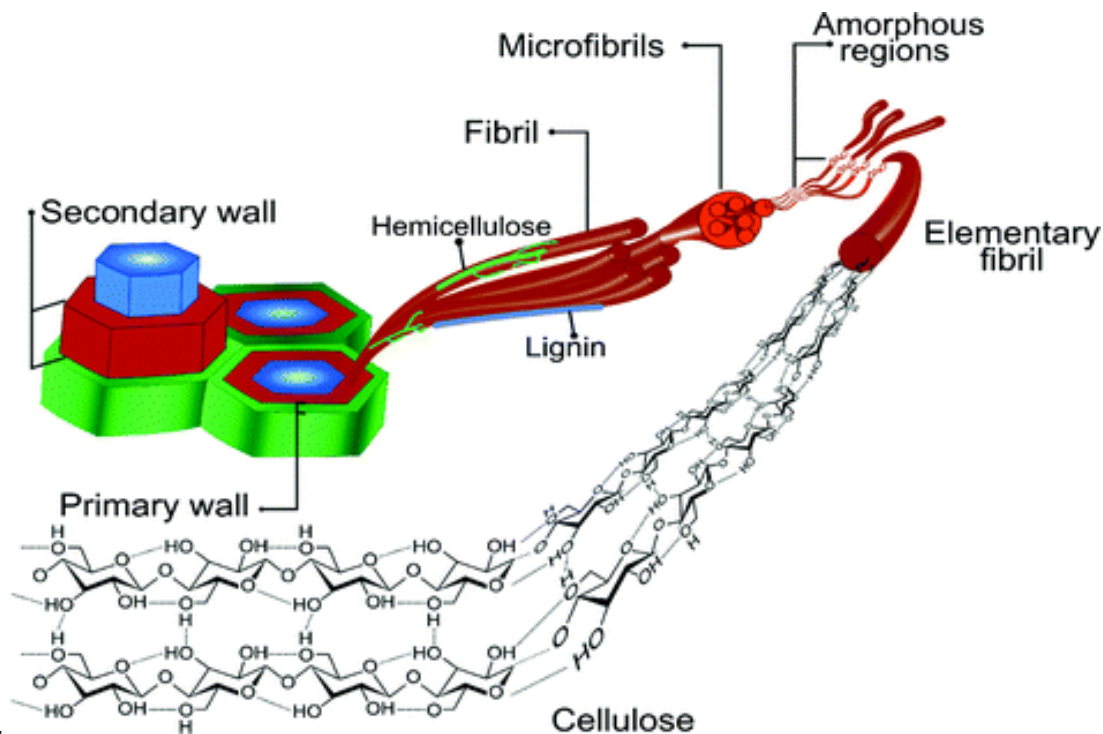


Figure 1.2. Morphology of hemp bast (Rojas et al., 2015)

The fiber bundles are obtained from the stems, which lie under the cortex, though most fibers come from the middle lamella of the stem (Adesina et al., 2020). The fiber bundles are glued together with chemical components such as lignin and pectin. The root of the hemp plant can extend to 50-80cm deep in the soil. The primary and secondary fibers are found in the top and bottom portion of the stem. The content of lignin in the secondary fiber is higher than that of primary fiber; therefore, secondary fibers are more strongly held together in the hemp stem (Sáez-Pérez et al., 2020).

1.5. Chemical Composition of Hemp

The hemp bast (*Cannabis Sativa* L.) as a natural fiber has been used primarily in the paper and textile industries (Thygesen et al., 2006). The hurd, which is normally the woody core of the hemp is used for extracting cellulose or as an energy source (Gümüşkaya et al., 2007). Hemp stems contain about 20-40% bast fibers and 60-80% hurds. Hemp bast fiber consists of cellulose (57-77%), hemicellulose (9-14%), and lignin (5-9%), pectin (1.6%), and others including fats and waxes (3.3%). Hurds comprises cellulose (40-48%), hemicellulose (18-24%), lignin (21-24%), and others (6-8%) including pectin, fats, and waxes (Dupeyre & Vignon, 1998; M. Kostic et al., 2008; Stevulova et al., 2014).

1.5.1. Cellulose

Cellulose is the most abundant organic material on our planet. Cellulose based materials have been used for thousands of years in clothing and as a building and energy resource (Sundarraaj & Ranganathan, 2018).

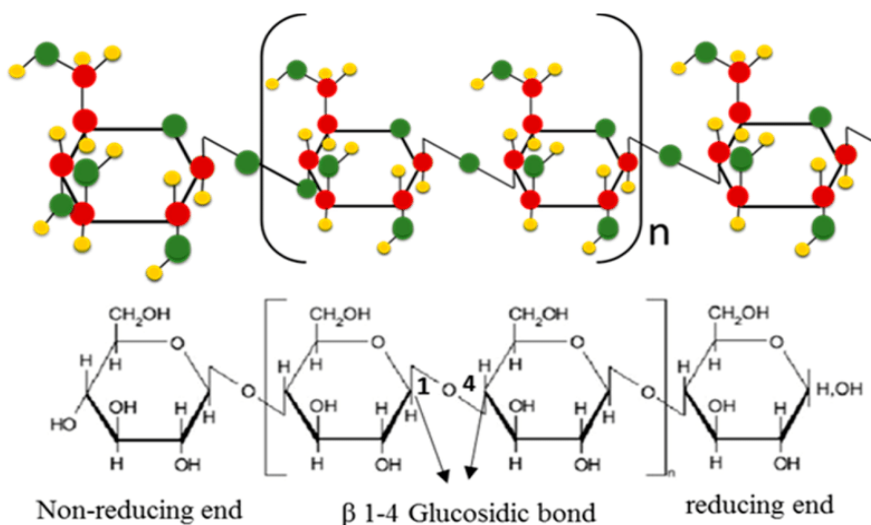


Figure 1.3. 3D structure of cellulose and beta 1,4 glycosidic bonds of cellulose (Rajinipriya et al., 2018)

However, the chemistry of cellulose is more recent having first been described by Anselme Payn in 1838 (Hon, 1994). Cellulose consists of both amorphous and crystalline

regions and acts as supporting material to keep the plants and trees erect (Gauss et al., 2021).

Figure 1.3 represents the 3-dimensional structure and the β (1, 4) glycosidic bonds of cellulose.

Figure 1.4 illustrates how cellulose, lignin, and hemicellulose are linked together in the hemp plant.

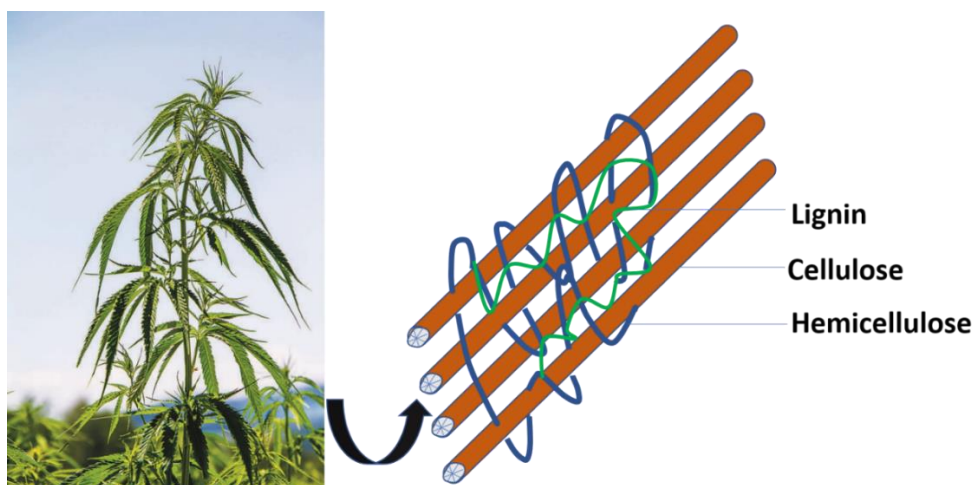


Figure 1.4. Hemp plant structure (Naidjonoka et al., 2020)

1.5.2. Hemicellulose

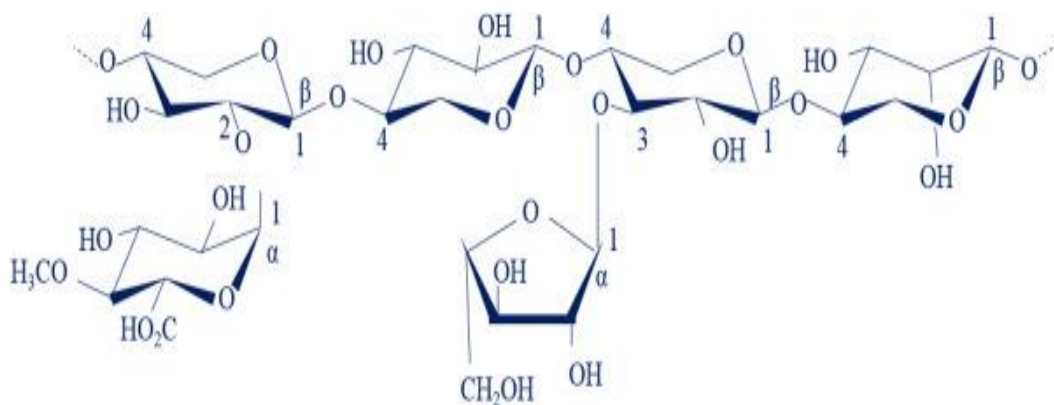


Figure 1.5. Structure of hemicellulose (Benaimeche et al., 2020)

Hemicellulose is a branched polysaccharide with the linear backbone bonded with the β (1,4) glycosidic linkages. As shown in figure 1.5, unlike cellulose, hemicellulose is full of amorphous regions and consists of short polymer chains.

1.5.3. Lignin

As can be seen in figure 1.6, lignin is a complex polymer of aromatic and aliphatic components.

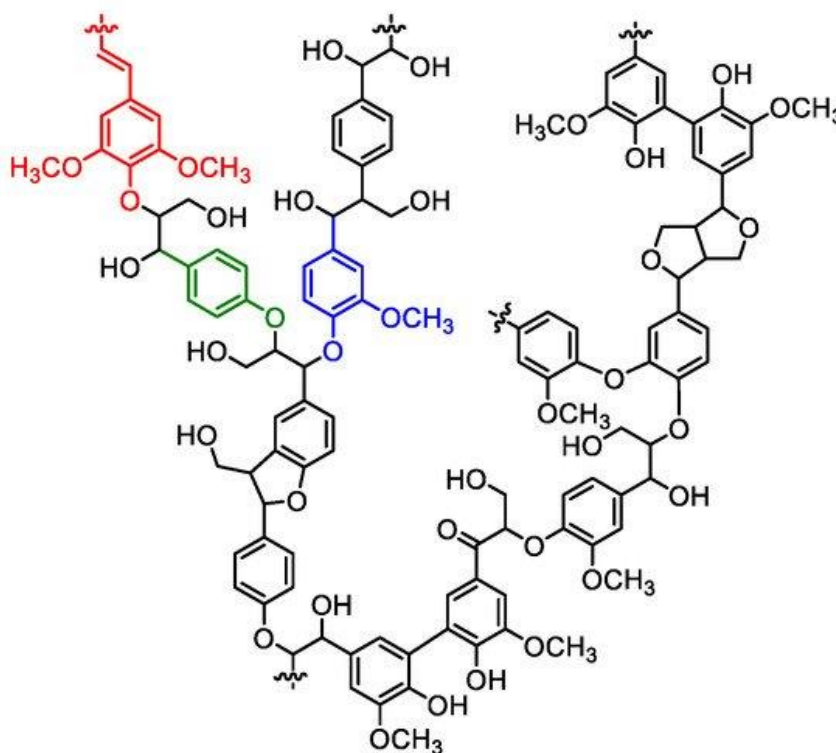


Figure 1.6. A possible structure of lignin. (red, blue, and green monolignols represent sinapyl alcohol, guaiacyl alcohol, and *p*-coumaryl alcohol, respectively) (Karunarathna et al., 2020)

1.6. Global Market of Hemp

Lignin is located throughout the middle lamella, primary cell, and secondary cell wall of the plant. Lignin and hemicellulose are responsible for making the stiff structure of fibers since they aid to form a matrix sheath structure around the fibers and microfibrils; thus, fibers achieve a high compression strength.

As a highly sustainable and ecofriendly crop, the hemp market doubled globally from 2016 to 2020. The mainstream production of hemp for research or commercial purposes is

ongoing in more than 47 countries. Since 2011, hemp cultivation has increased significantly in terms of tonnage and acreage worldwide (Johnson, 2014).

The US is the largest importer of hemp products and obtains seeds and fiber from the countries such as China and Canada. Additionally, the US government has authorized hemp production for research and commercial purposes under the Agricultural Act-2014. This resulted in hemp production increasing rapidly throughout the US (Johnson, 2014; Quaicoe et al., 2020).

According to the report published by Market Data Forecast, the industrial hemp market is anticipated to increase by 13.7% from 2020 to 2025, and the market worth will be 12.98 Billion USD (“Industrial Hemp”, 2021).

1.7. Applications of Hemp in Textiles

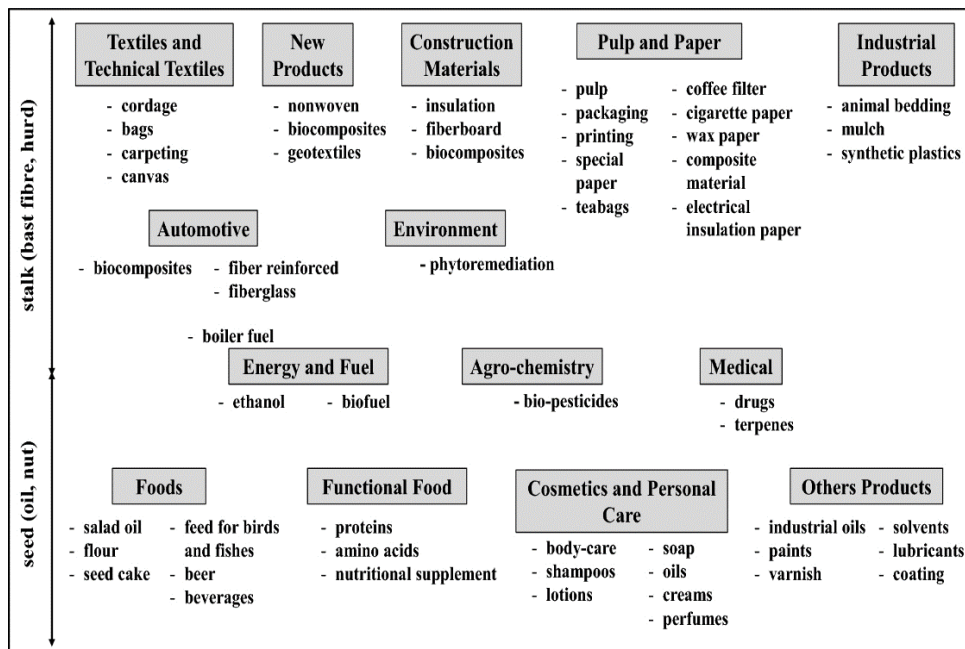


Figure 1.7. Use of hemp in different sectors (Morin-Crini et al., 2019)

Hemp fiber has been used for thousands of years to manufacture yarns, rugs, ropes, canvas, and fabrics. Woven or knitted hemp fabrics have been chosen due to their durability and strength (Misnon et al., 2015). An advantage of hemp fiber is that it has higher tensile strength

than other natural fibers such as cotton, ramie, jute, etc. The versatility of hemp fiber has attracted attention all over the world. Historically, hemp was an essential fiber material in the navy, including shipping, clothing, and fishing, etc.

At present, hemp is a billion-dollar market and has immense prospect in textile applications such as sportswear, jeans, bags, cushions, hats, socks, etc. (“Industrial Hemp” 2019). The good thermal and biodegradable qualities of hemp, along with UV resistance properties and antimicrobial properties make it a lucrative fiber material. According to the literature, hemp possesses good hygienic properties, including anti-allergic properties, anti-microbial, and UV resistance properties (Crini et al., 2020). An illustration of the applications of hemp is represented in figure 1.7.

CHAPTER 2. LITERATURE REVIEW

2.1. Traditional Degumming Methods of Hemp Fibers

Hemp stems must undergo a pretreatment process after harvesting to get high-quality hemp fibers to manufacture the superior composites and textile products. The pretreatment process enables hemp fibers to be separated from the woody portion of the hemp stem. Sticky compounds such as lignin, pectin, and waxes are mainly responsible for binding the hemp fibers to the non-fibril compounds; therefore, it is an ultimate goal to remove the gummy materials from the hemp stem to obtain fiber bundles and individual fibers (Idler et al., 2011; Ribeiro et al., 2015). In addition, it is essential to remove gummy materials from the hemp stem to enhance the hydrophobicity of its cellulosic components.

The removal process of adhesive compounds from the stem is referred to as a retting or degumming process. The traditional methods of hemp fiber defibrillation are water and field retting. Over the past few years, researchers have focused on developing a controlled and efficient way to get higher quality fibers for further hemp fiber processing and applications. Traditional methods of degumming hemp have some disadvantages; thus, researchers have been focusing on other ways to process hemp fibers such as chemical, mechanical, and enzymatic pretreatments. However, the selection of the retting process is highly dependent on the main requirements of the end-uses and the geographical location of hemp production (Horne, 2020).

2.1.1. Field Retting

Field retting is also known as dew retting. In this process, stems are cut into the desired length and spread over the field, and the natural dew soaks stems during the night (Horne, 2020). The hot temperatures of the day and the moisture during the night, along with a high relative humidity, allow fungi (*Penicillium* and *Aspergillus*) and natural bacteria (*Clostridium* and

Bacillus) to grow on the hemp stems. Hydrolytic enzymes are secreted from these microorganisms, which act as the fermentation entities that enable the degradation of the pectic substrates and hasten the defibrillation process to make hemp fiber bundles or individual fibers (Dhakal & Zhang, 2015; Mazian et al., 2020; Ribeiro et al., 2015). Additional secreted enzymes from these microorganisms also allow the degradation of waxes, starches, and fats from the hemp plant cells (Horne, 2020).

The time span of the field retting process ranges from 2-8 weeks depending on weather, location, and the extent of retting required (Bleuze et al., 2020; Horne, 2020). The degree of retting can be identified by the external colors of the hemp stems; a dark grey color of hemp stems is defined as the occurrence of retting due to the activities of the microorganisms. It is possible to check out the degree of retting by the manual inspection of fibers' defibrillation from the woody part of the hemp stems (Horne, 2020). Field retting offers many advantages in that it consumes less water than other enzymatic and chemical treatments. Field retting is a cheap process since there is minimum or no energy inputs required and it offers an efficient agricultural procedure by saving labor costs (Bacci et al., 2011).

However, field retting has several disadvantages since it is affected by specific climatic conditions; thus, this process is feasible only in particular regions where the weather allows for these microorganisms to proliferate (Liu et al., 2015). For example, field retting is scarcely applicable in Italy due to its high-temperature weather; on the other hand, Northern Europe has comparatively mild temperatures facilitating microbial activities (Assirelli et al., 2020). Dew-retting produces uneven fibers and affects the quality of individual fibers (Assirelli et al., 2020). This type of field retting is not controllable. Land has to be used for an extended period which is

an inefficient agricultural practice (e.g., this process delays the sowing of the next crop in the same field) (Henriksson et al., 1997; Liu et al., 2015).

Liu and his co-workers found that the mechanical properties, chemical composition, and morphology of USO-31 hemp cultivars were varied with the period of field retting and harvesting duration (2015). Low mechanical properties and cellulose content were found due to the field retting of hemp both for early and late harvesting. This is not desirable, especially for textile applications and hemp fiber-reinforced composites. Furthermore, the degradation rate of pectin substrates was reduced due to the low accessibility of microorganisms into the hemp stem throughout the field retting (Liu et al., 2015).

2.1.2. Water Retting

Water retting is a method by which the finest hemp fibers are produced within a short time. The conventional way of water retting is to steep hemp stem in streams, ditches, canals, or rivers. However, this submersion procedure has been replaced by the use of water tanks in which there is a flow of running water which is controlled mechanically. Water retting tanks can be open or sealed as per the climatic conditions and might be arranged in a series or cascade layout. The temperature of water tanks usually is controlled between 30-40°C, which allows the growth of *Pectinolytic* bacteria. *Bacillus* sp. are mostly dominant in the first 40 hours, but when the oxygen is depleted, *Clostridium* sp. thrive in the anaerobic conditions, and these bacteria are mainly responsible for the degradation of pectin compounds (Nair et al., 2013; Zheng, et al., 2020).

In comparison, water retting has several advantages over dew/field retting because water retting functions in a more controlled environment and yields good quality fibers. Furthermore,

water retting does not require appropriate arable land and is a quicker process to treat the hemp stem (requires only a few weeks) (Small & Marcus, 2002).

However, water retting is inhibited by the fact that there are contaminants created and it consumes a vast amount of freshwater (Bleuze et al., 2018; Jankauskienė & Gruzdevienė, 2013), increases production costs and creates large amounts of fermentation waste. Though the practice of water retting still continues in some parts of the world, the addition of chemicals, enzymes, and microorganisms to the water retting treatment to compensate for the environmental pollutions ultimately is making this pretreatment process of hemp more expensive (Dhakal et al., 2007).

2.1.3. Fungal Degumming

Fungi acts as a decomposer in most ecosystems and are widely used for the hydrolysis of wood materials. Many white-rot fungi have been chosen selectively for the degradation of lignin, which is getting a lot of interest in the paper and textile industries for the pretreatment process of biomass (e.g., pulping and bleaching) of woody and non-woody materials (Law et al., 2020).

In terms of degradation ability, the white-rot fungi are classified into two groups: one group is capable of degrading the lignocellulosic materials (lignin, hemicellulose, and cellulose) through oxidative and hydrolytic processes approximately at the same rate; the other group can perform selective delignification (only targeted lignocellulosic materials of the biomass through the production of extracellular oxidases) (Halis et al., 2012). In this context, the most effective and vital enzymes are laccases, manganese peroxidases, and lignin peroxidases, which are capable of phenolic and non-phenolic lignin degradation.

Thus, white-rot fungi could be used as an agent to delignify the lignocellulosic materials by removing only non-cellulosic materials. The fungal treatment of hemp fibers has potential, as

an efficient, low-cost, environmentally sustainable solution. However, the fungi species have to be selected meticulously because some fungi groups can consume/degrade the cellulose by removing glucose from the fiber structures (Law et al., 2020).

It is vital to control several factors which affect fungal growth, such as pH, moisture, temperature, oxygen and carbon sources (as an energy source), and nitrogen for the nucleic acid synthesis, amino acids, and protein. For example, the growth of white-rot fungi is limited to the temperature range of 25°C to 30°C within a wide pH range. A study by Pickering et al. reported that the fungal treatment of hemp fibers with/without alkali treatment had a better bonding strength (22% increment for only fungal treatment and 32% increment for combined fungal-alkali treatment) when hemp fiber was reinforced with polypropylene composites than the untreated hemp reinforced polypropylene composites (2007).

2.1.4. Chemical Treatment

Another traditional degumming method of natural fiber is the exploitation of various chemical agents to remove non-cellulosic materials to manufacture high-quality fibers for end-use purposes.

A major drawback of natural cellulosic fibers is hydrophilicity, which is caused by the presence of the hydroxyl groups in its lignocellulosic materials. However, hydroxyl groups of the crystalline region of cellulose are sturdily linked and inaccessible. The hydroxyl groups of the amorphous region are feebly linked with the fiber structure, and they are free to react with the chemical agents (Kabir et al., 2013).

Chemical agents can be applied as a cleaning catalyst for purging the hemp fiber surface by removing non-cellulosic compounds; these agents allow for a more homogeneous glucose surface. Cleaned fibers have more adhesive strength allowing for further textile processing

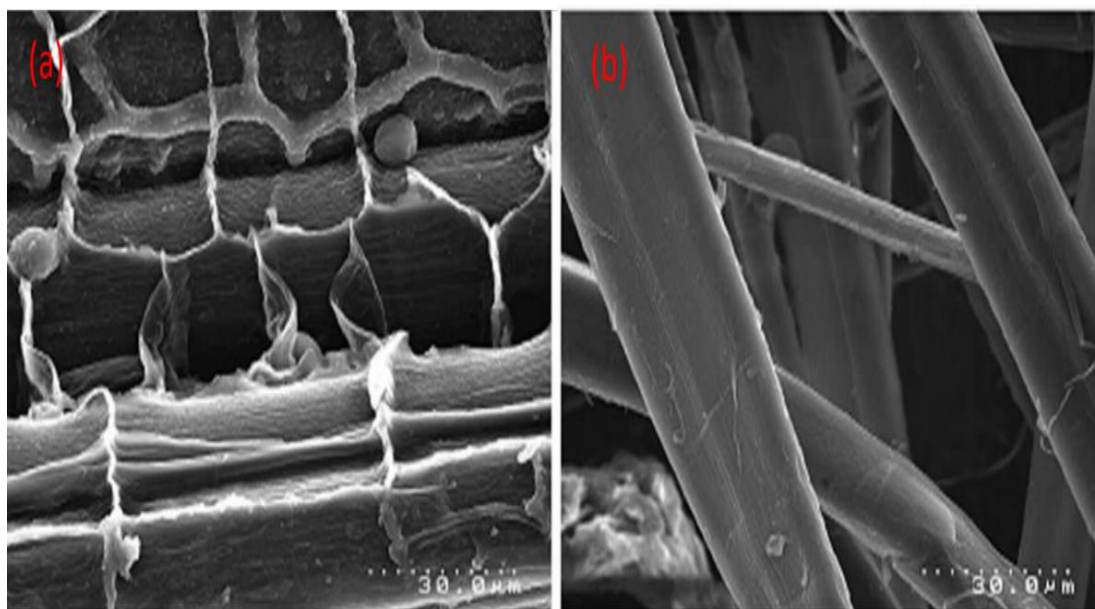
(textile dyeing and good quality hydrophobic garment products) and high-quality hemp fiber reinforced composites due to the improved polymer-matrix adhesion (Sawpan et al., 2011). Furthermore, the removal of pectin eases the fiber separation and increases the free surface area for the chemical bonding in subsequent textile processing steps (Le Troëdec et al., 2011).

Studies have been done on several chemicals and strategies, including alkali treatment, acetylation, bleaching, salinization, benzylation, and many other treatments using organic and inorganic acids, peroxide, chelating agents, anhydrides, sodium chlorite, and sodium sulfite (Barczewski et al., 2020; Hubbell & Ragauskas, 2010; Kabir et al., 2020; Kostic et al., 2010; Le Troëdec et al., 2009; Menghini et al., 2021; Oladele et al., 2020). However, different approaches/treatments have different degrees of effluent and impurity generation and have caused damage either to the chemical composition of hemp fibers or their structure.

Even though chemical treatments are able to make the finest quality of fibers, they have caused several negative impacts on the environment by generating a high amount of effluent and requiring high energy inputs which have resulted in increased production costs. These reasons have influenced the introduction of biological treatments of hemp fibers. However, replacing chemical treatments with the biological treatments alone cannot produce appropriate outputs/effects on the finished treated individual hemp fibers as hemp contains only around 57-77% cellulosic compounds (Stevulova et al., 2014). Therefore, until now, chemical treatments, especially alkalization, have been considered as the most efficient and direct way of removing non-cellulosic materials to improve the fiber quality of hemp (Parvez et al., 2021; J. Zhang et al., 2014).

2.1.5. Alkali Treatment

Alkali treatment is a popular chemical pretreatment process for natural fibers. Over the past decades, alkali treatment has been used to improve the properties and investigate the structures of natural fibers. Treatment with alkali is an established and well-known method to remove non-cellulosic materials from the fiber wall of cellulosic fibers, especially hemicellulose and lignin, enhancing the cellulose reactivity toward fiber and matrix adhesion in terms of composite reinforcements (Vijay et al., 2019).



A.1

A.2

Figure 2.1. SEM image of untreated hemp fibers (A.1), SEM image of alkali-treated hemp fibers (A.2)(Islam et al., 2011)

Sodium Hydroxide is the most commonly used alkaline agent, and it removes amorphous materials from the hemp fiber surface (Le Troëdec et al., 2011), and thus, it enhances the hydrophobicity of the hemp fiber. Figure 2. 1 shows the surface morphology of hemp fibers

before and after alkali treatment. Table 2.1 represents an estimation of the chemical composition of hemp fibers before and after alkali treatment.

Table 2.1. Cellulose, lignin, and ash content of hemp fiber samples (Islam et al., 2011)

Fibers	Cellulose (%)	Lignin (%)	Ash (%)
Untreated hemp	63.3	4.5	2.6
Alkali-treated	96.7	0.3	0.2

Previous research has shown that modest treatment of alkali brings increased crystallinity of cellulose, and it might happen due to the removal of non-cellulosic constituents from the fiber (Sunny et al., 2020). On the other hand, a stringent treatment with alkali is responsible for converting crystalline cellulose to amorphous cellulose (Kabir et al., 2012; Sawpan et al., 2011). Many studies have been done on the alkali treatment effect of hemp fibers with varying parameters (Kabir et al., 2012a; Kabir et al., 2012b) (e.g., high-temperature treatment and ambient temperature treatment). However, there is limited information on the direct comparison of ambient and high-temperature alkali treatment on the tensile properties of individual hemp fiber. Ambient temperature provides several advantages, such as low processing cost, simplicity of the process, and a large volume of hemp fibers can be treated (Sunny et al., 2020). Furthermore, other studies have reported that alkali treatment has increased moisture sorption (Ahmad et al., 2018; Lazić et al., 2018), electrical resistance (Kostic et al., 2010), and reduction in water retention power (Lazic et al., 2017).

2.1.6. Delignification Treatment

Several methods have been developed for the delignification of biomass. The most common and popular method to delignify the biomass is the Kraft process, which is used in the paper and pulp industry (Dessbesell et al., 2020). Alkaline peroxide is used to remove lignin and hemicellulose from biomass; though this process is considered an eco-friendly method (Hubbell

& Ragauskas, 2010; Sun et al., 2004), it has a disadvantage in that peroxide radicals could damage the cellulose structure.

Sodium chlorite is another commonly used chemical agent to delignify natural fibers. Pretreatment of the natural fibers with the sodium chlorite acts as a bleaching agent. However, pretreatment of natural fibers with the acid-chlorite (an aqueous solution of sodium chlorite and acetic acid) also affects the polysaccharides and cellulose (Kumar et al., 2009). The degradation of cellulose is due to the chlorite effect (oxidative degradation of polysaccharides) and/or acid hydrolysis (acidic cleavage of glycosidic bonds) (Hubbell & Ragauskas, 2010). Therefore, acid-chlorite treated fibers lose their tensile strength, and it would negatively impact the final textile product.

Another pretreatment of hemp fiber is the alkaline boiling process in which sodium chlorite and sodium hydroxide are applied with hemp fibers at boiling temperature to remove the lignin and pectin from the fiber. However, Wang et al. (2003) reported that the removal of pectin and lignin is highly dependent on the concentration of the solution. Still, lignin could not be fully removed because of the cross-linking and aromatic structure of lignin (Wang et al., 2003).

2.1.7. Enzymatic Treatment

The enzymatic treatment is another potential and eco-friendly process for the surface modification of natural fibers. This treatment takes place under mild conditions, which is highly dependent on the selection of enzymes; the enzyme-mediated reaction accelerates the non-disruptive transformations of the fiber surfaces. Basically, cellulase catalytic action is responsible for cleaving the β (1,4) glucoside bonds through enzymatic hydrolysis into separate cellulose molecules, yielding individual fine fibers. Two major groups of enzymes are reported to treat natural fibers: (a) hydrolases-glycosidases, proteases, and lipases, and (b)

oxidoreductases-tyrosinase, laccase, and peroxidase. Cellulase and hemicellulase are employed to modify fibers used in textile industries (Buschle-Diller et al., 1999). Lignin peroxidases and manganese peroxidases are used in an acidic medium (pH 4-6) for the removal of lignin from the lignocellulosic materials (Pickering et al., 2007), while alkaline pectinase needs an alkaline medium to remove pectin from the natural fibers (e. g. pectinase has high activity under alkaline medium with the degradation of cellulose of hemp fibers) (Dijkstra, 2018).

It was reported from past research that the combination of different enzymes and methods have better results in terms of the removal of lignin, hemicellulose, and pectin from hemp fibers. For instance, the combination STEX (Steam Explosion) and pectinase treatment of hemp fibers yielded up to 78% cellulose (Terzopoulou et al., 2015; Thygesen et al., 2006). The combination of a silane coupling agent and pectinase yields improved tensile properties with increased hydrophobicity in the resulting hemp-polypropylene composites (Li et al., 2017).

However, this process needs strict control to minimize fiber strength and weight loss, and hydrophilicity. Enzymatic treatment has several disadvantages, such as it needs expensive enzymes, equipment and technologies, and special treatment of the produced wastewater.

2.2. Physical and Thermomechanical Treatment of Hemp Fibers

2.2.1. Steam Explosion

The steam explosion process (STEX) is the combination of a thermal, mechanical, and chemical treatment in which chemical reagents and steam penetrate into the fiber bundles due to high pressure and temperature. Mechanical breakdown of lignocellulosic materials is caused by the heat energy and explosive decompression, and simultaneously, modification of lignocellulose happens through the hydrolysis of hemicellulose, lignin structure alteration, resulting in a

reduction of the crystallinity index (Bismarck et al., 2002; Cui et al., 2012; Donatelli et al., 2017; Gurunathan et al., 2015; Jacquet et al., 2015; Nykter, 2006; Sutka et al., 2013).

Some researchers have shown that the STEX treatment could remove lignin under oxidative conditions as carboxylic acids and low molecular phenolic compounds (Gravitis et al., 2011). It has been reported that the treatment of hemp fibers by STEX coupled with a hydrothermal process and wet oxidation could increase cellulose content (86-90% by weight) (Thomsen et al., 2006).

STEX treatment of the sodium percarbonate-soaked ramie fibers had a residual gum content below 5% (by weight of fiber) and a breaking tenacity of 5.4 cN/tex, and the fiber fineness was higher than 6.25 d/tex (Jiang et al., 2018).

2.2.2. Plasma Treatment

Plasma treatment of hemp fibers under low temperature and atmospheric pressure can modify the chemical structure of the fiber which improves the wettability and dyeability of the fibers by producing a rough fiber surface (Dasong, 2015; Radetic et al., 2007; Radetić et al., 2009). A one minute plasma treatment of hemp fibers under atmospheric pressure can alter the shear-strength (Baltazar-y-Jimenez et al., 2008) due to the generation of new functional groups and removal of contaminants through the increased fiber surface roughness. However, longer plasma treatment of fibers can lower tensile strength, Young's Modulus, and elongation at break. Hemp fibers subjected to plasma treatment under atmospheric pressure dielectric barrier discharge (time-120 seconds, power discharge between 40-80W) had a reduction of hemicellulose and lignin content that was up to nine times and five times respectively as compared to that of hemicellulose and lignin content of raw hemp (Pejić et al., 2020).

2.2.3. High Energy Radiation Treatment

Lignocellulosic materials can be modified by high-energy radiation utilizing accelerated electron beams or gamma radiation. However, varying doses of radiation can cause the degradation or depolymerization of the materials through the alteration of irradiated lignocellulosic material and enhancement of oxygen-containing functional groups resulting in chemical reagents easily accessing the crystalline region of cellulose. Until recently, little research has been conducted on the application of high-energy radiation, especially on hemp fibers. It was reported that xylan was more sensitive than the cellulosic part of the hemp fibers, and higher doses of electron beam irradiation with/without 1% sodium hydroxide or hot water had a higher chemical decomposition rate due to the chain scission of hemp samples (at the doses of 150, 300, and 450kGy) (Shin & Sung, 2008; Sung & Shin, 2011).

2.2.4. Ultrasonic Treatment of Hemp

Ultrasonic treatment of hemp fibers for 24 hours shows a promising effect on the degradation of hemicellulose 243. Recently Singh et al. (2020) found that ultrasound-assisted alkali-urea treatment at a sonication time of 10, 15, and 20 minutes, alkali (NaOH) concentration of 2. 3.5, 5 % (w/v), and urea-concentration of 1, 1.75, and 2.5% (w/v) could remove lignin selectively. The treated biomass had a higher thermal stability, crystallinity index and smaller crystallite size (Singh et al., 2020).

2.2.5. Microwave Energy Treatment

2.2.5.1. Fundamentals of Microwave Heating

Microwave is electromagnetic radiation in the spectrum between 300 and 300000 MHz, a region that lies between radio frequencies and infrared and corresponds to wavelengths of 1cm to 1m (Banik et al., 2003; Motasemi & Ani, 2012). Most microwave reactors (commonly used for

chemical synthesis reaction) and domestic microwave ovens are operated at the frequency of 2.45 GHz or around 900 MHz to avoid the cellular phone and telecommunication frequencies. In contrast, other frequencies are reserved by the Federal Communications Commission to use for industrial, scientific, and medical purposes (Huang et al., 2020; Kappe et al., 2012; Kostas et al., 2017; Nüchter et al., 2004).

Microwave heating occurs through two main mechanisms: one is to induce rapid heating when microwaves contact with polar molecules and ions, the other involves ionic conduction and dipole rotation. Dipole rotation occurs when polar molecules attempt to realign themselves with the vacillating electric field of microwaves (Hippel & Morgan, 1955). During dipole rotation interactions, energy is released in the form of heat through dielectric loss and molecular friction (see figure 2.2) (McKendry, 2002). Most importantly, microwave heating is the opposite of conventional heating (conventional heating refers to the heat transfer toward a comparatively cooler region of the particular material by the thermal conduction) as illustrated in figure 2.2. Therefore, microwave heating can be referred to as the conversion of energy instead of a form of heating, in which electromagnetic energy is converted into heat (Motasemi & Afzal, 2013; Tao et al., 2020). There are several advantages of this inverse microwave heating, such as improved energy transfer efficiency and the achievement of the desired temperature in a short period of time. In addition, microwave heating offers better control of the heating process, eradicates the risk of overheating of the samples as the heating process is instantaneous; thus, it could be a potential and useful technique for the drying of wet materials (Palma et al., 2020), especially for the industrial pretreatment process where heating is an exigent parameter. Microwave heating has been utilizing for the pretreatment of biomass since many years due to its efficient heating system.

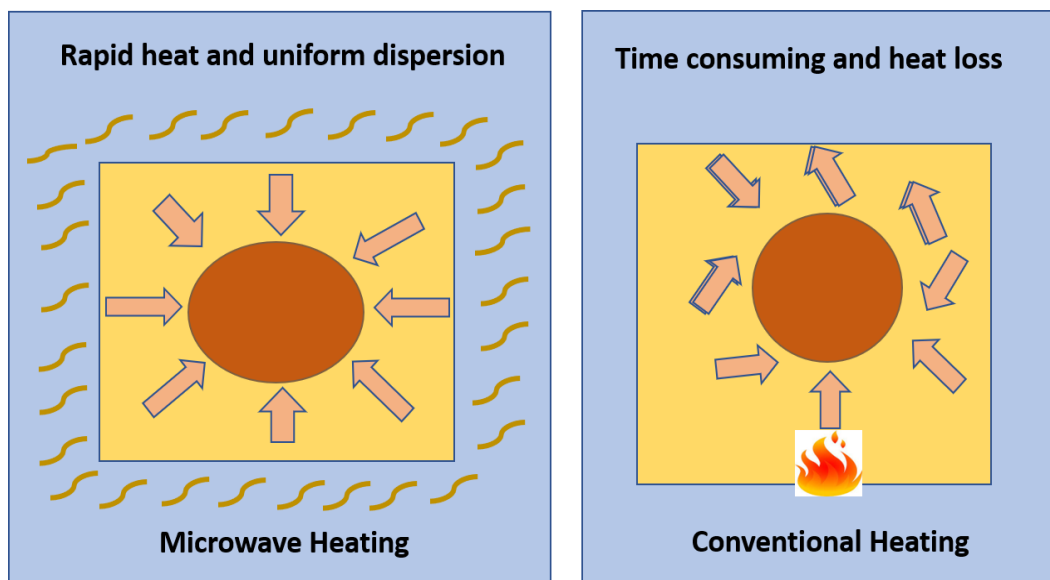


Figure 2.2. Microwave and conventional heating mechanism

Over the past few years, a list of pretreatment technologies have been applied for the processing of biomass, including steam explosion (Appusamy et al., 2021; Chen & Liu, 2015; Sahota et al., 2017), ultrasound assisted processing (Esmaeilzadeh Kenari & Dehghan, 2020; Ji et al., 2021; Körlü & Bahtiyari, 2021; Nargotra et al., 2020; Ong & Wu, 2020), ammonia fiber expansion (Gao et al., 2014; Hoover et al., 2014; Mathew et al., 2016; Smuga-Kogut et al., 2021; J. Zhao et al., 2020), and extrusion (Duque et al., 2017; Han et al., 2020; Moro et al., 2017; J. Zheng & Rehmann, 2014). Microwave heating provides a reliable and alternative solution toward applications where energy conversion is necessary by avoiding the traditional thermal conduction systems (Antonetti et al., 2012). Rapid heating rates can be achieved, which is an important factor for the alternative type of chemistry (it is unique because of the internal heating phenomenon) (Ai et al., 2020).

2.2.5.2. Microwave-Assisted Degumming

It is necessary to presoak fiber samples to degum them with the assistance of microwave heating for few hours to get a better degumming effect as presoaking allows fibers to absorb the water,

and it helps to remove pectin and lignin in the subsequent treatment (Nair et al., 2015; Ruan et al., 2020). It is reported that 30 min of microwave heating could have a high pectin removal rate as compared to non-pres soaked flax fiber (Zhao Ji et al., 2020).

Though the practice of microwave heating is not typical for natural fibers, these days, this heating is getting a lot of attention due to its process efficiency. Zhao, Ji et al. found that the microwave-assisted hot water degumming of flax fiber rate was 1.33 times higher than natural hot water retting with similar tensile properties for both processes (2020).

2.3. Deep Eutectic Solvent

2.3.1. Fundamentals of Deep Eutectic Solvents

Deep Eutectic Solvent (DES) was first reported as a green solvent by (Abbott et al., 2003). DES could be synthesized by the combination of two or three components where a certain ratio of hydrogen bond acceptors (HBA, e.g., quaternary ammonium salts, choline derivatives, organic acids) and hydrogen bond donors (HBD, e.g., amides, polyols, and carboxylic acids) is needed.

Table 2.2. Classification of DES

Formula	Components	Terms
$Cat^+ X^- \times z MCl_x$	Quaternary halide + metal chloride	M= Zn, Sn, Al, In X= Cl, Br
$Cat^+ X^- \times z MCl_x \times y H_2O$	Quaternary halide + metal chloride hydrate	M = Cr, Co, Cu, Fe X = Cl, Br
$Cat^+ X^- \times z RZ$	Quaternary halide + hydrogen bond donor	Z = CONH ₂ , COOH, OH X = Cl, Br
$M Cl_x + RZ = (MCl_{x-1})^+ \times RZ + (MCl_{x+1})^-$	Metal halide hydrate + hydrogen bond donor	M = Al, Zn X = Cl, Br Z = CONH ₂ , OH

The eutectic solution has a freezing point that is significantly lower than the melting

points of the individual components in the mixture. One of the prime advantages of DES is that it offers similar physiochemical properties to ionic liquids and is even more sustainable, cheaper, and has a lower toxicity than ionic liquids (Alkhatib et al., 2020).

Table 2.3. Physical properties of some DESs at 298K (if it varies, it is specified in the table) (Jablonský & Šima, 2019).

HBA/HBD, Molar Ratio	Freezing Point (°C)	Viscosity (cP)	Density (gcm ⁻¹)	Conductivity (mScm ⁻¹)
ChCl/U, 1:2	12	750	1.25	0.75
ChCl/U, 1:2	12	169 (40 °C)		0.199(40°C)
ChCl/Me-U, 1:2	29			
ChCl/1,3-Me ₂ -U, 1:2	70			
ChCl/CF ₃ CONH ₂ , 1:2		77 (40 °C)	1.342	
ChCl/EG, 1:2	-20	37	1.12	7.61
ChCl/EG, 1:3		19 (20 °C)		
ChCl/Gly, 1:2	-40	376	1.18	1.18
ChCl/Gly, 1:3		450 (20 °C)		
ChCl/D-Fru, 1:2	4			
ChCl/D-Glu, 1:2	14			
ChCl/phenol, 1:3			44.6	3.14
ChCl/phenol, 1:3			28.2 (35 °C)	4.77 (35 °C)
ChCl/phenol, 1:3			19.2 (45 °C)	6.77 (45 °C)
ChCl/1,4-butanediol, 1:3		140 (20 °C)		
ChCl/1,4-butanediol, 1:4		88 (20 °C)		
ChCl/imidazole, 3:7		15 (70 °C)		12 (60 °C)
ChCl/acetamide, 1:2	51			
ChCl/MalA, 1:1	10	721		0.55
ChCl/MalA, 1:2	22	1124		
ChCl/valeric acid, 1:2	33			
ChCl/mandelic acid, 1:2	34			
ChCl/OxA, 1:1				

Generally, DES is prepared by one of four methods such as a heating method, a grinding method, an evaporation method, or a freeze-drying method (Jablonský et al., 2019). The heating method consists of mixing and heating the components at around 100°C with constant stirring until a homogeneous and transparent solution is prepared; it could take about 60-90 min (Kumar et al., 2016).The grinding method consists of mixing the components at room temperature and

grinding until a homogenous solution is prepared (El Achkar et al., 2019). The evaporation method uses a rotary device and the obtained liquid is kept in a desiccator (containing silica gel) until a constant weight is gained (Yiin et al., 2016). The freeze-drying method is prepared through the lyophilization of the aqueous solution of individual DES components (Alvarez-Vasco et al., 2016). However, this method is rarely used as the water cannot be evaporated fully, and water acts as part of the DES network. Different types of DES are presented in the table 2.2. Therefore, different DES can be used for different desired properties of the final products. Choline Chloride is one of the most widely used components of the eutectic solution. Choline chloride is a quaternary ammonium salt that is cheap and biodegradable; it can be extracted either from biomass or synthesized from fossil fuels.

Hydrogen bond donors such as urea, renewable carboxylic acids, polyols, and amides (they are considered safe hydrogen bond donors) can be used with choline chloride to prepare green eutectic mixtures. The use of those chemicals provides an advantage by avoiding the metal compound in the eutectic network/system; hence, it can be utilized in several fields, such as biotechnological and biochemical processes (Jablonský & Šima, 2019).

2.3.2. DES-Assisted Degumming

It has been reported in the literature over the last two decades, that DES is considered as a novel alternative form of ionic liquid with the properties of biodegradability and cheap cost. It has been attractive to researchers, and applied in many fields such as electrochemistry, extraction processes, catalysis, organic synthesis, and dissolution (Loow et al., 2017; Song, Jiang, et al., 2019). DES has been used in the pretreatment process of biomass or natural cellulosic fibers. One of the most significant advantages of DES is that it can extract lignin from cellulosic fibers with little or no damage to the cellulosic structure of the fibers, which is the first and foremost criteria to enhance the mechanical properties of cellulosic fiber-based end-products (Lim et al., 2019). Recently Nie et al. studied the degumming process of kenaf fibers using combined DES coupled with microwave and alkaline-ultrasonic treatment (2020). The treatment created a clean fiber surface (the extracted residual gum content was 9.419%), improved fiber fineness (4.125 tex), and breaking tenacity of 13.650 CN/tex (Nie et al., 2020). Song, Jiang et al. (2019) found that Steam Explosion (STEX) coupled with DES to treat the ramie fibers was comparable with the traditional alkali degumming method in terms of the reduction of residual gum content (4.68%), improved fiber fineness (1419.99 Nm), and higher breaking tenacity of 5.98 cN/dtex.

However, the conductivity and viscosity of DES are inversely related. The lower viscosity of DES allows it to act as an effective solvent and aids in degrading the chemical compositions of biomass (Kumar et al., 2016). For instance, DES made of choline chloride and carboxylic acids can easily penetrate into the hardly accessible structure of biomass. It is reported that DES prepared by choline chloride and carboxylic acids has a lower removal rate of lignocellulosic components than the DES made of choline chloride and lactic acid for the treatment of palm oil fruits (Tan et al., 2018).

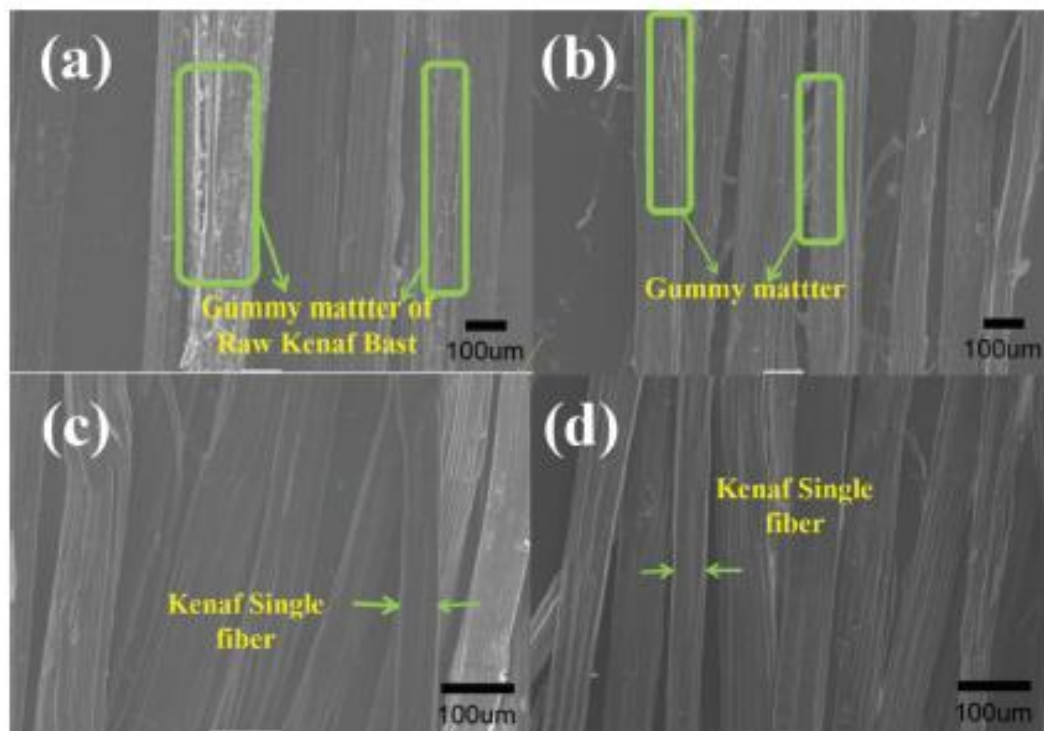


Figure 2.3. SEM image of raw kenaf bast, combined microwave-DES degummed kenaf fibers, microwave-DES-ultrasonic degummed kenaf fibers, and chemically degummed kenaf fibers (Nie et al., 2020)

Hydroxyl groups, amino groups, and carbonyl groups are varied in different types of DES. However, these diverse properties of having different groups facilitate the fractionization (lignin) or delignification of biomass due to the breakage of the ether bonds of lignocellulosic materials.

2.4. Research Gap

- Extremely limited research has been conducted on sustainable degumming of hemp fibers.
- None of them addressed effective removal of gummy compounds.
- Literature involved costly, non-biodegradable, time consuming, and complex pretreatment processes of hemp fibers.

2.5. Significance of the Study

- USA is one of the largest exporters and importers of hemp-based products.
- Textile contaminants are a direct threat to the environment.
- Making use of green DES solvent and convenient microwave energy.
- Understanding the underlying mechanism of gummy material removal from the hemp fiber structure.
- Developing a water-free method to degum hemp fibers.
- Approaching an economic, biodegradable, and easier way of hemp fiber pretreatment process.

2.6. Research Question

- Could the Combined Microwave Energy and Deep Eutectic Solvent (DES) treatment have a comparable or better degumming effect on hemp fibers than the traditional degumming method in terms of removing gummy materials and improved mechanical and thermal properties?

2.7. Objectives of the Study

Hemp is a natural cellulosic fiber. It is attractive for textile applications as an alternative to the mostly used cotton or synthetic fibers and as a composite reinforcement agent due to its low cost, good mechanical properties, low density, biodegradability, and sustainability. Hemp bast fiber exhibits a high tensile strength (300-800 MPa), a low density (0.150 g/cm³ to 1.64g/cm³), and high stiffness (30-60GPa) (Silva, 2015).

Furthermore, hemp fiber-based textile products exhibit Ultra-Violet (UV-ray) protecting properties, inherent natural resistance against the degradation occurring due to mold and mildew,

and has higher tearing and wearing strength (Grifoni et al., 2009; Olaru et al., 2016; Thompson et al., 1998; Y. Zhang et al., 2020).

To enhance the above-mentioned properties, the degradation or removal of gummy compounds from the middle lamella-fiber bonding is necessary to attain fiber bundles and/or individual hemp fibers. However, the removal of non-cellulosic materials from the structure of hemp fibers increases glucose molecules resulting in higher crystallinity cellulose which enhances tensile strength and fineness, and improves the hydrophobicity and adhesion between fiber and matrix in the stemming composites.

As far as fiber extraction is concerned, conventional methods of degumming are time-consuming and hinges on the weather conditions of the hemp production region (for water and field retting) or creates detrimental environmental issues (the use of toxic chemicals for the chemical treatment of hemp). The controlled environment and the selection of bacteria which secretes the proper enzymes to degrade the non-cellulosic components needed for enzymatic treatments requires a large power consumption, which increases the cost of fiber production.

Traditional solvents for lignin extraction from the lignocellulose include alkali solvent, organic solvents, and dilute acids which can dissolve the lignin and its remains. These solvents have posed different negative impacts such as high toxicity, requiring high temperature and pressure in the process which increases production costs (Kumar & Sharma, 2017; Xue et al., 2016). Ionic liquids have avoided these disadvantages but are expensive and complex to synthesize in the empirical applications for delignification (e.g., biorefinery). In this context, DES has received attention since it has the desired properties to overcome the above-mentioned disadvantages (Ma et al., 2018). This solvent can efficiently solubilize lignin and its fragments and hemicellulose (Hong et al., 2020), which is the ultimate goal to achieve high-quality fibers

and facilitates improved physical, chemical, and mechanical properties. Microwave heating has exhibited its potential to removing gummy components from the lignocellulosic materials/natural fibers with/without the addition of other pretreatment processes. Furthermore, microwave energy has been considered as a less time-consuming and sustainable practice of heating with minimum energy inputs.

Therefore, the use of microwave energy and DES has been seen as a promising, biodegradable, sustainable, eco-friendly, and less time-consuming method, with a lower production cost for the extraction of hemp fibers.

Chapter 3. Methodology

3.1. Materials and Method

3.1.1. Materials

Raw hemp fibers were obtained as a gift from Colorado, US. Choline chloride (pure > 98%) was purchased from TCI America, Portland, OR, US, Urea (crystallized) was procured from VWR BDH CHEMICALS, Radnor, PA, US, Sodium sulfate (anhydrous) was acquired from VWR Life Science, Ohio, US, Sodium metasilicate was purchased from BTC Beantown Chemicals, Hudson. NH, US, Sodium hydroxide (ACS-grade Pellets) was bought from Fisher Chemical, Fair Lawn, NJ, US, Sodium polyphosphate (pure) was purchased from ACROS Organics, NJ, US, and Hydrogen peroxide-30% (aqueous solution of ACS reagent grade) was supplied by J.T. Baker, US.

3.1.2. Preparation of Raw Hemp Samples



Figure 3.1. Hurds free raw hemp fibers

The woody core (hurds) from the fibers was removed manually as shown in figure 3.1 before all the experimental uses. It was kept at room temperature for two weeks before degumming the fibers.

3.1.3. Preparation of Hemp Fibers by Traditional Alkali Degumming Treatment

Cleaned raw hemp samples were cooked at 90°C for one hour with a 1% NaOH solution in an oil bath and the liquor ratio was 1:20 (volume/weight) (Jiang et al., 2018). After boiling, the hemp fibers were washed with cold-water five times to achieve neutrality. The recipe for the alkali degumming includes 1% sodium hydroxide (NaOH), 3% hydrogen peroxide (H_2O_2), 3% sodium polyphosphate (NaPO_3), 2% sodium sulfate anhydrous (Na_2SO_4), 3% sodium metasilicate (NaSiO_3), and 3% urea ($\text{CH}_4\text{N}_2\text{O}$). The liquor ratio of the alkali degumming was 1:20, and all the chemicals were weighed according to the weight/volume ratio.

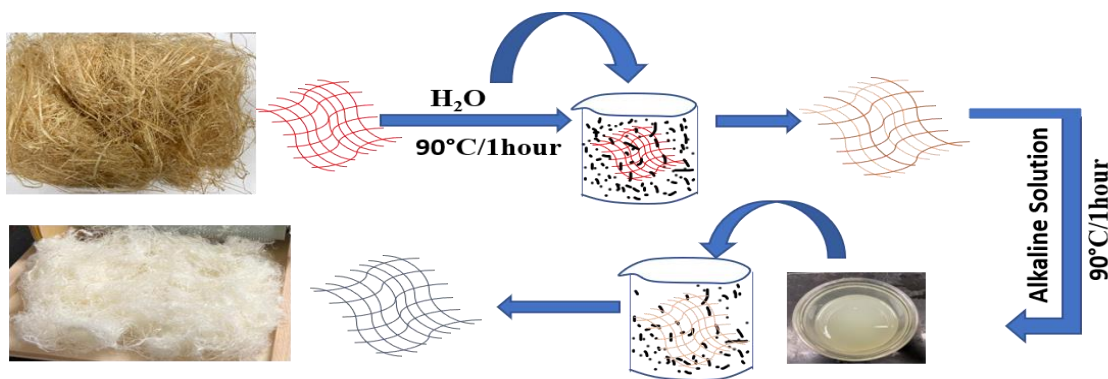


Figure 3.2. Schematic of alkali degumming process

After cooking with the abovementioned recipe for one hour in the oil bath at 90°C, the hemp fibers were washed with cold-water five times to achieve neutrality and dried in an oven at 60°C. The dried fibers were kept for further characterizations.

3.1.4. Combined Microwave Energy and Deep Eutectic Solvent (DES) Degumming

3.1.4.1. Synthesis of Deep Eutectic Solvent (DES)



Figure 3.3. Deep eutectic solvent (DES)

DES was synthesized from the mixture of the choline chloride and urea at a molar ratio of 1:2 (figure 3.3). The mixture was heated at 80°C and stirred magnetically for 1.5-2.5 hours in the oil bath until a transparent and homogenous solution was obtained. Choline chloride and Urea were used without further purification.

3.1.4.2. Combined Microwave and DES Degumming

The hurds-free hemp samples were submerged into the DES solution in a 90 mL Teflon vessel.

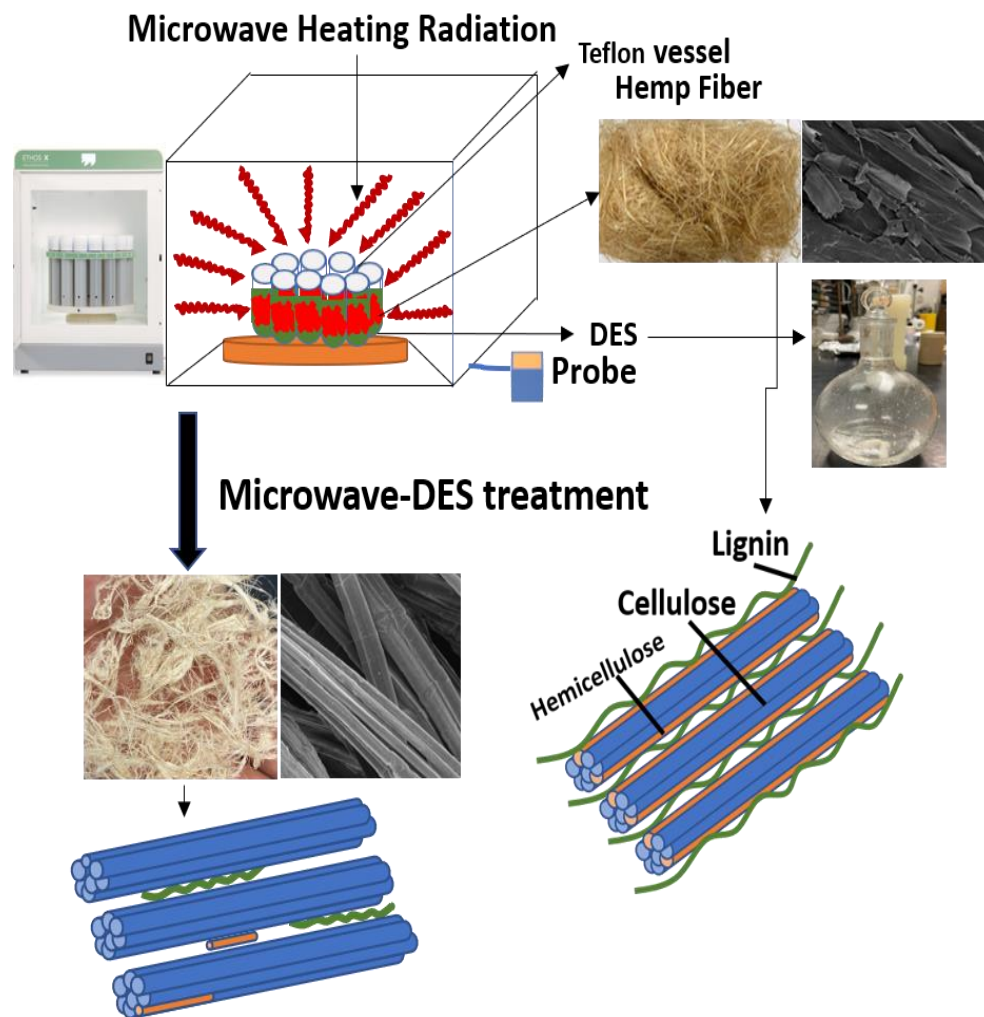


Figure 3.4. Schematic of hemp fiber degumming using combined microwave energy and DES

Table 3.1. Settings and Conditions of different treatments of hemp fibers

Fiber: DES	Temperature (°C)	Time (min)	Power Level (kW)	Stirring (%)	Samples Name
1:10	100	60	1000	24	DES-1s-1:10
1:20	120	90	1000	24	DES-1s-1:20
1:20	150	130	1000	24	DES-1s-1:20 (150°C×130min)



A.1



A.2



A.3



A.4

Figure 3.5. Microwave-DES treated fibers at a solid liquor ratio of 1:10 (A.1), 1% NaOH treated fibers after Microwave-DES treatment at 1:10 ratio (A.2), Microwave DES-treated fibers at 1:20 solid-liquor ratio (A.3), 1% NaOH+1% H_2O_2 +3% Urea treated fibers after Microwave-DES treatment (A.4).

The microwave extraction system (model: Ethos X, Milestone, The World of Microwave Chemistry, North America) was provided by the School of Renewable Natural Resources at Louisiana State University. The power and stirring level of the microwave extraction system were 1000kW and 24%, respectively.

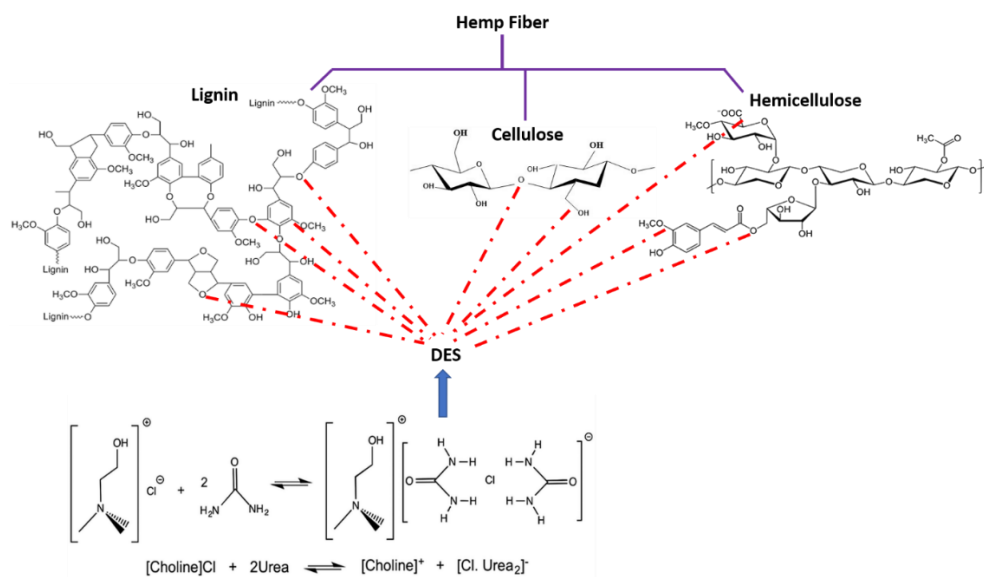
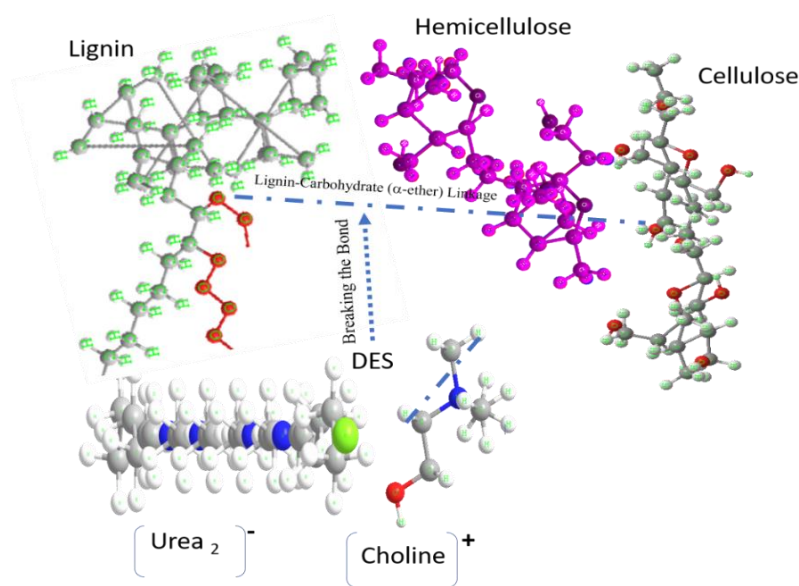


Figure 3.6. Extraction of lignin from hemp fiber structure by DES (A.1 and A.2)

After degumming the hemp fibers in the microwave extraction system as shown in figure 3. 5, fibers were washed with cold water, oven-dried, and kept for further characterization.

3.1.4.3. Alkali Treatment of the Combined Microwave-DES Treated Hemp Fibers

Table 3.2. Conditions of alkali treatment

Samples	Treated Sample Connotation	Recipe	Final Alkali-treated Sample Connotation	Treatment Conditions
Microwave-DES treated at 1:10 (100C*60min)	DES-1s-1:10	1% NaOH (w/v)	DES-2s-1:10	90°C×60min
Microwave-DES treated at 1:20 (120C*90min)	DES-1s-1:20	1% NaOH (w/v), 1% H2O2 (w/v), 3% Urea (w/v)	DES-2s-1:20	90°C×60min

Microwave-DES treated hemp fibers were further subjected to an alkali treatment with the following recipe in table 3.2. After the alkali treatment of the Microwave-DES treated fibers, the hemp fibers were washed with cold-water and oven-dried. The samples were stored for further analysis and characterization.

3.2. Characterizations

3.2.1. Fiber Surface Morphology

Hemp fiber surface (both degummed and undegummed) morphology was investigated by using a high-performance electron microscope (Model-JSM-6610 LV SEM, JEOL, Japan) in a high vacuum condition at an accelerated voltage of 5kV. Before scanning, the samples were cut into small pieces and coated with a thin layer of gold using an EMS550X sputter coater.

3.2.2. Fourier Transform Infrared Analysis (FT-IR)

Fourier Transform Infrared analysis (FT-IR) of hemp fibers (both degummed and undegummed) was performed to identify the presence of free functional groups (Moghaddam & Mortazavi, 2016). FT-IR spectra were obtained using a Bruker Alpha & Tensor 27 FT-IR

spectrophotometer and OPUS software. The operating conditions were as follows: 32 scans per sample, resolution of 4 cm^{-1} , with a wave-length range of $400\text{--}4000\text{ cm}^{-1}$. There was no need to prepare the samples to scan in the spectrophotometer.

3.2.3. X-Ray Diffraction (XRD) Analysis

Hemp powdered fibers (both degummed and undegummed) were analyzed by X-ray diffraction using a PANalytical Empyrean X-ray Diffractometer (Malvern, UK) equipped with the PreFIX modules (Fast interchangeable X-ray). The diffractometer was operated at 40mA and 40kV with the $K\alpha$ -1 wavelength of 1.540598, $K\alpha$ -2 wavelength of 1.54426, Cu-anode material, scan range of 5-50, and scan step size of 0.0131303 to get the diffraction patterns of both raw and degummed hemp fibers.

3.2.4. Thermal Analysis

3.2.4.1. Thermogravimetric Analysis (TG)

Thermogravimetric analysis was performed for both degummed and undegummed hemp fibers in a nitrogen atmosphere with a flow of 40ml/min by using a TG analyzer (Model-Q50, TA Instruments Inc., New Castle, DE, US) at a heating rate of $10^{\circ}\text{C}/\text{min}$ up to 600°C at room temperature. All samples were about 20 mg and kept in the platinum crucible. TGA and Derivative TGA curves were obtained as a function of weight and temperature to investigate the thermal degradation of hemp fibers.

3.2.4.2. Differential Scanning Calorimetry Analysis (DSC)

DSC measurement was conducted with a Q10 DSC (TA Instruments Inc., New Castle, DE, USA) and operated at a 40 ml/min sample purge flow rate under a nitrogen atmosphere. Fiber samples were heated from 30°C to 540°C at a heating rate of $20^{\circ}\text{C}/\text{min}$. All samples were about 5 mg.

3.2.5. Chemical Composition Analysis

The Solid-State NMR test of both treated and untreated hemp fibers was carried out using a 3-channel Bruker AV-400 (Bruker BioSpin, Billerica, MA) equipped with the 400 MHz spectrophotometer. These solid-state instruments were fitted with Z-axis gradients. The conditions for one-directional (1D) cross-polarization magic angle (CP/MAS¹³C NMR) were as follows: MAS rate-10kHz, 4096 Scans, relaxation delay-2s, and CP contact time-2ms.

NMR data was analyzed and processed with the Topspin Software (version-2.1) (Bruker), Origin Pro (2021 version), and dmfit (NMR@CEMHTI) software. The obtained data from Topspin and Origin software were processed by utilizing Gaussian/Lorentzian models through dmfit software to obtain chemical compositions of both degummed and undegummed hemp fibers.

3.2.6. UV-Vis Spectrophotometer Analysis and UV Shielding Property

3.2.6.1. UV-vis Analysis

A UV-vis spectrophotometer (Evolution 350, Thermo Scientific, US) was used to investigate the UV-shielding performance of both degummed and undegummed fibers according to the Australia/New Zealand (AS /NZS 43 99) standard. Sample fiber films of treated and untreated hemp fibers were made at 100°C using a pressing machine (GRIMCO PRESSES INC.) with an applied pressure of 4000 psi. Fiber films were scanned with the spectrophotometer equipped with an integrating sphere at a wavelength range of 290-400nm and a slit bandwidth of 1 nm. Transmittance was recorded at 5 nm intervals.

3.2.6.2. UV Protection Factor (UPF)

UV protection factor is regarded as the protection efficiency of fibers or fabric from UV radiation. A higher and lower UV protection factor (UPF) value is defined as fibers or fabric's

higher and lower protection level from the UV radiation, respectively. UPF was calculated by using below equation 1.

$$UPF = \frac{\sum_{290}^{400} E_{\lambda} S_{\lambda} \Delta_{\lambda}}{\sum_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda} \Delta_{\lambda}} \quad (1)$$

Where E_{λ} = CIE Erythral spectral effectiveness, S_{λ} = Solar Spectral irradiance for a typical summer day, T_{λ} = Spectral transmittance of fibers, Δ_{λ} = Wavelength Step.

Table 3.3. UPF classification system

UPF range	Protection Category from UV radiation	Effective UVR transmission %	UPF ratings
15-20	Good Protection	6.7-4.2	15, 20
25-39	Very Good Protection	4.1-2.6	25, 30, 35
40-50, and 50+	Excellent Protection	≤ 2.5	40, 45, 50, 50+

The UPF results of various samples were discussed according to the Australia/New Zealand standard (AS /NZS 43 99) and table 3. 2 which provides the various UPF classification of UV shielded clothing categories.

Chapter 4. Results and Discussion

4.1. FT-IR Analysis

FT-IR spectra were used to investigate the presence of the functional groups of both raw and degummed hemp fibers. The band of FT-IR spectra at 894 cm^{-1} is ascribed to the β (1-4) glycosidic bonds of cellulose in the polysaccharides (Kalisz et al., 2021). The symmetric vibration in the plane of C-O-C glycosidic linkages appeared at the band of 894 cm^{-1} for all the hemp samples as can be seen in figure 4. 1 (Kubovský et al., 2020). It signifies that the structure of cellulose has undergone little change in all the treated hemp fibers. The stretching of ester groups and carbonyl groups (C=O) of hemicellulose and lignin were recognized at the band of 1741 cm^{-1} (Liu et al., 2007). The disappearance of the peak at 1741 cm^{-1} for all the degummed hemp fibers indicted the removal of hemicellulose from the fiber structure (Stevulova et al., 2014; Zhang et al., 2005). The characteristic peak of lignin was observed at the band of 1624 cm^{-1} (C=C stretching of the aromatic ring). However, the peak was weakened after alkali treatment, stretched and shifted a little bit for the DES treatment at 1:10 ratio, and gradually reduced and disappeared after the DES treatment at 1:20 ratio, which was a clear indication of the removal of lignin (Fang et al., 2017; Y. Wang et al., 2015). The bending of methylene carbons ($-\text{CH}_2$) of lignin and hydroxyl groups ($-\text{OH}$) in-plane bending were observed at the 1424 cm^{-1} and 1376 cm^{-1} bands, respectively. Those two peaks appeared as straight and stretched in the treated fibers. The changes in the characteristic vibration peaks of raw hemp fibers at 2916 cm^{-1} and 1741 cm^{-1} indicated that chemical modification had occurred in the DES-treated fibers (Le Troëdec et al., 2009). The absence of the peak at 2831 cm^{-1} in the DES-treated samples signaled the removal of oil and waxes from the hemp fibers after degumming (Stevulova et al., 2014) except for the DES-1s-1:10 sample.

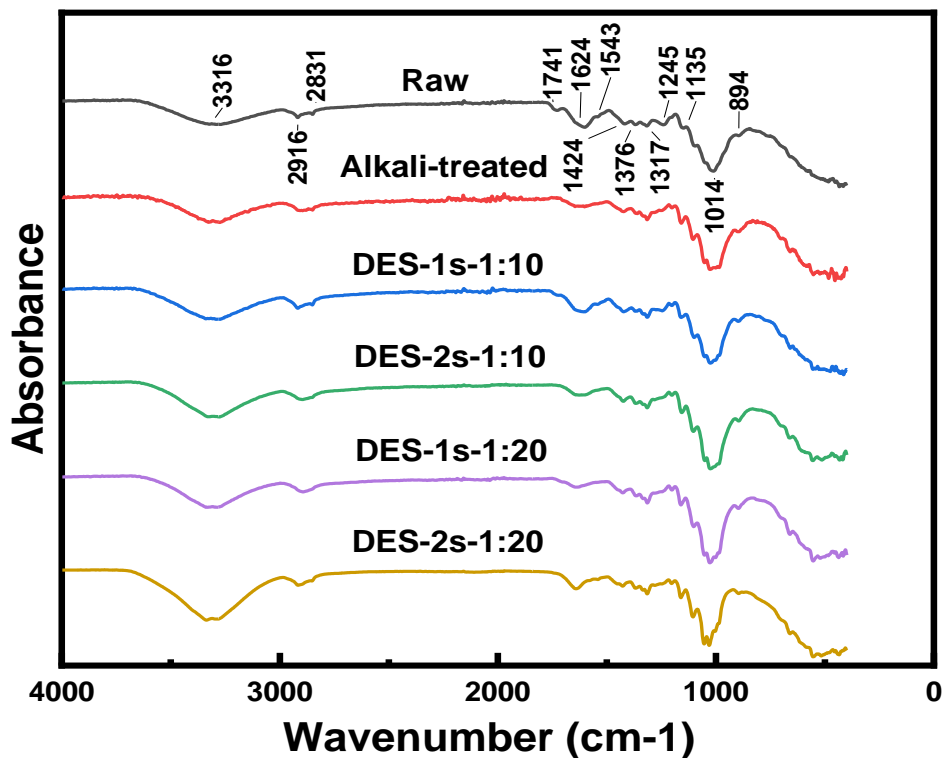


Figure 4.1. FT-IR spectra of both degummed and undegummed hemp samples

Table 4.1. Wavenumbers of FT-IR spectra of both degummed and undegummed hemp samples and assignment of the functional groups

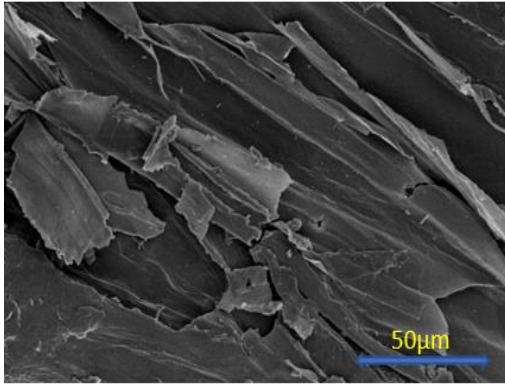
Wavenumber (cm ⁻¹)	Functional Group	Assignment
3316	OH stretching	Polysaccharides
2916	C-H symmetrical stretching	Polysaccharides
1741	C=O stretching	Hemicellulose
1624	OH (water)	Cellulose
1543	C=C aromatic ring symmetrical stretching	Lignin
1376	CH bending	Cellulose
1317	CH ₂ Wagging	Cellulose
1245	CO stretching	Lignin
1135	C-O-C asymmetric stretching	Cellulose
1014	C-C, C-OH, C-H vibrations of side groups and ring	Hemicellulose
894	Glycosidic linkages symmetric ring stretching	Polysaccharides

The vibration absorption peak of hydroxyl groups at the band of 3316 cm⁻¹ was getting stronger and stretched for both alkali and microwave-DES treated samples due to the reaction that occurred between DES solvent and the fiber (for the DES-treated fibers), and sodium

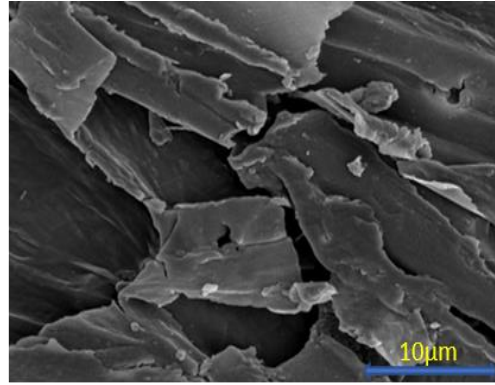
hydroxide and the fiber (for the alkali treatment) (Kostic et al., 2008; Wang et al., 2003). The functional groups assignment of FT-IR spectra wavenumbers of degummed and undegummed hemp fibers are represented in table 4.1.

4.2. SEM Analysis

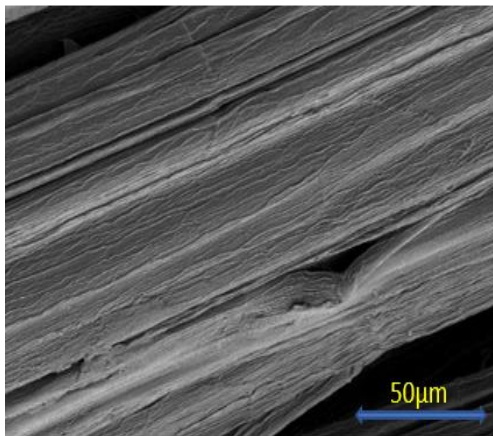
The SEM images revealed the surface morphology and degumming effect of treated and untreated hemp fibers. It was obvious that the raw hemp fiber as shown in figure 4.2A.1 and figure 4.2A.2 contain lignin, hemicellulose, oil, waxes, and pectin which resulted in the SEM images illustrating a rough and stiff fiber surface. However, alkali-treated hemp fiber had a noticeably clear fiber surface, due to the removal of lignin from the fiber structure (Kabir et al., 2013). The clear and smooth surface of alkali-treated fibers revealed good individual fibers with the whitened effect, which was due to the use of NaOH and H₂O₂ (H₂O₂ and NaOH are responsible for removing lignin and destruction inherent chromophores present in the raw hemp fibers) (Rani et al., 2020). Furthermore, aqueous solution of hydrogen peroxide acts as an eutectic mixture therefore the depression of boiling point accelerates the degumming process of hemp fibers with a low process temperature in the alkaline-peroxide solution (Kačer et al., 2012). As the electron delocalization occurred in the conjugated double bonds of fibers allow to absorb visible light, therefore, a whitening effect can be found on the degummed fibers (M. Busch & K. Busch, 2019). As shown in figure 4.2E.1, E.2, F.1, and F.2, microwave-DES treated fibers showed an exceptionally smooth and clear surface. Even though DES-treated fiber at 1:10 ratio in figure 4.2E.1, E2 ratio had a comparatively lower transparent surface, this might suggest the presence of low content of gummy materials. However, after increasing the microwave heating temperature and DES: fiber ratio (SEM micrographs in figure 4. 2E.1, E.2 of DES-treatment at DES: fiber = 1:20 ratio), the hemp fibers represented a clean surface with a white



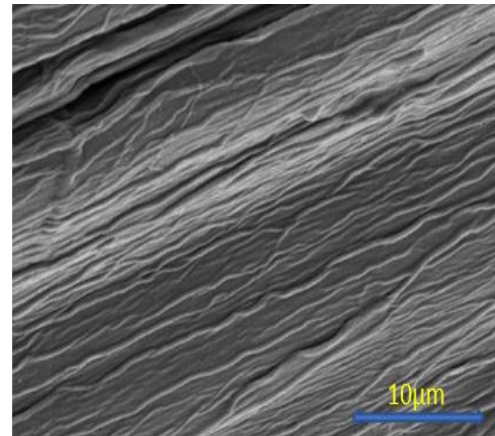
A.1



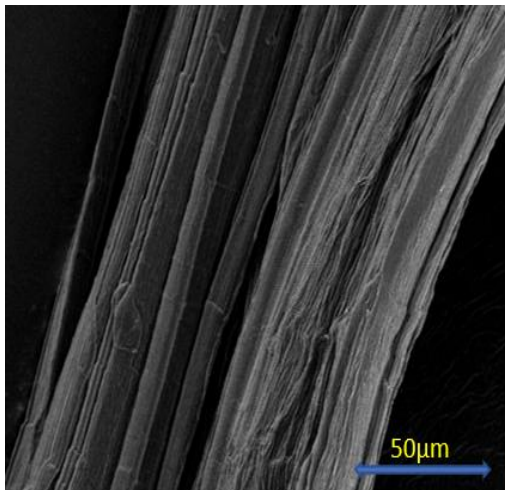
A.2



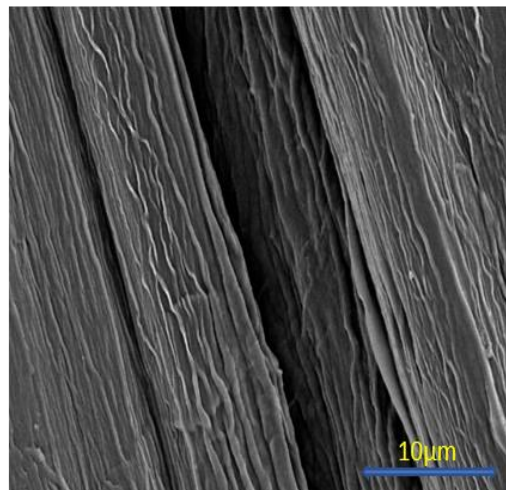
B.1



B.2

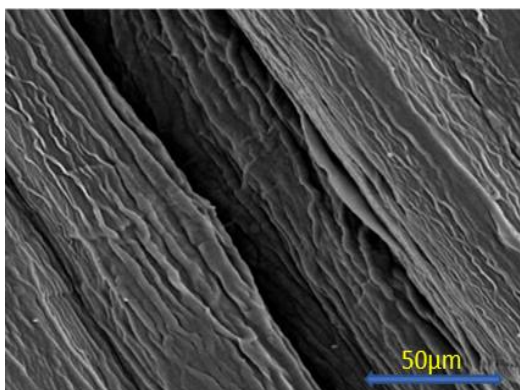


C.1

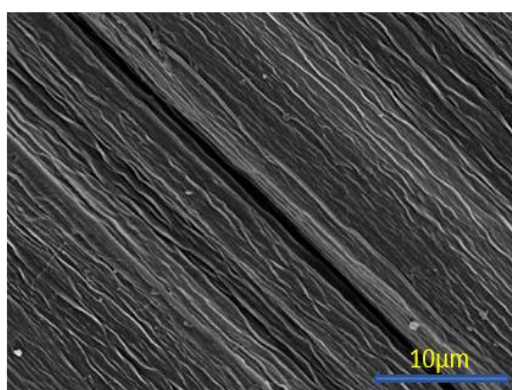


C.2

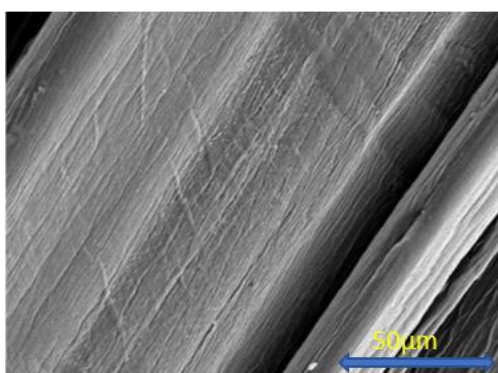
(fig. cont'd)



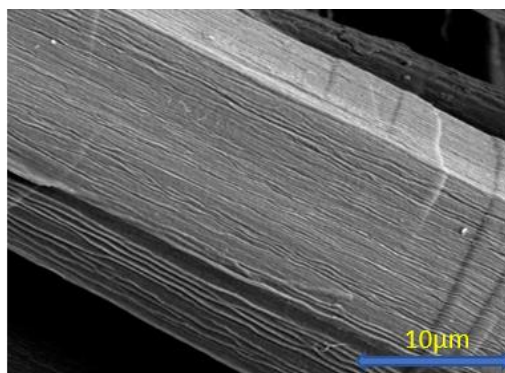
D.1



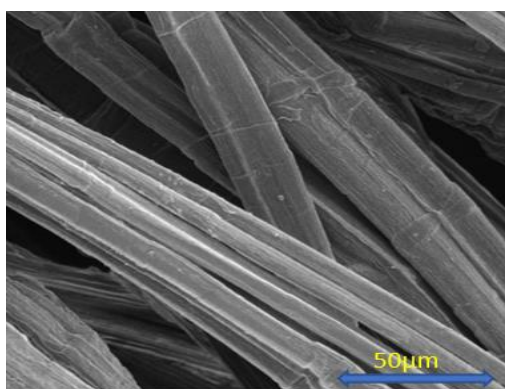
D.2



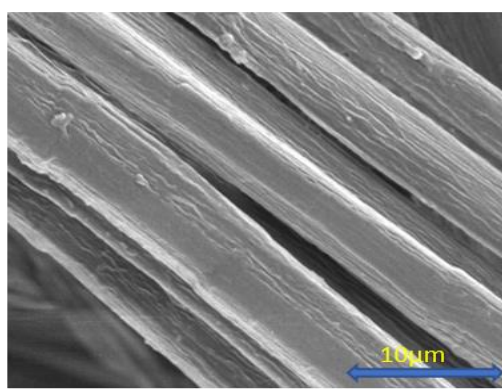
E.1



E.2



F.1



F.2

Figure 4.2. SEM images of both treated and untreated hemp fibers (A.1, A.2, B.1, B.2, C.1, C.3, D.1, D.2, E.1, E.2, F.1, F.2)

glowing appearance which was comparable with alkali treated fiber surfaces. In the literature, the degumming of hemp was studied at 150°C and reported that the fiber structure had some cracks

and pits (Shimpi, 2017). However, Microwave-DES treated fibers as can be seen in figure 4.2F.1 and 4.2F.2 had very few cracks and voids even after increasing the process temperature and time up to 120°C and 1.5 hours; this might be caused due to the uniform dispersion of microwave heating throughout the hemp fiber structure and low freezing temperature of DES (12°C). In addition, lignin is strongly linked by the hydrogen bonds and formed lignin-carbohydrate complexes. However, these strong hydrogen bonds can be weakened due to the formation of competing hydrogen bonds between the hydroxyl groups of lignin-carbohydrate complexes and the chloride ions of DES network (Liu et al., 2017); thus, lignin could be removed from the fiber structure. However, the H⁺ protons (from the hydrogen bond donor of DES) can selectively cleave the ester and/or ether linkages of lignin-carbohydrate complexes without the destruction of C-C bonds of cellulose, removing hemicellulose and lignin from the fiber structure (Alvarez-Vasco et al., 2017; Hou et al., 2018).

4.3. XRD Analysis

The crystallinity index of degummed and undegummed hemp fibers was analyzed using the Segal equation (equation 2) from the X-ray diffraction spectra (Segal et al., 1959).

$$CrI \% = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \quad (2)$$

Where I_{200} represents the maximum intensity of the lattice peak of 2θ angle at 24 degrees, which is imputed to the crystalline region. I_{am} denotes the intensity of 2θ angle at 18 degrees, concerning the amorphous region of cellulose (Efendy & Pickering, 2014). Average crystallite size from the XRD diffractograms was calculated by using the Scherrer equation (Equation 3) (Patterson, 1939; Scherrer, 1912; Shiraishi & Inagaki, 2003).

$$d = \kappa \lambda / \beta \cos \theta \quad (3)$$

Where d = average crystallite size in nm, K = Scherrer Constant = 0.94 for spherical crystallites,

λ = X-ray wavelength, Cu $K\alpha$ = 1.5406 angstrom, β = Line broadening at FWHM (Full-Width

Half-Maximum) in radians, θ = Bragg's angle in degrees, which is half of 2θ .

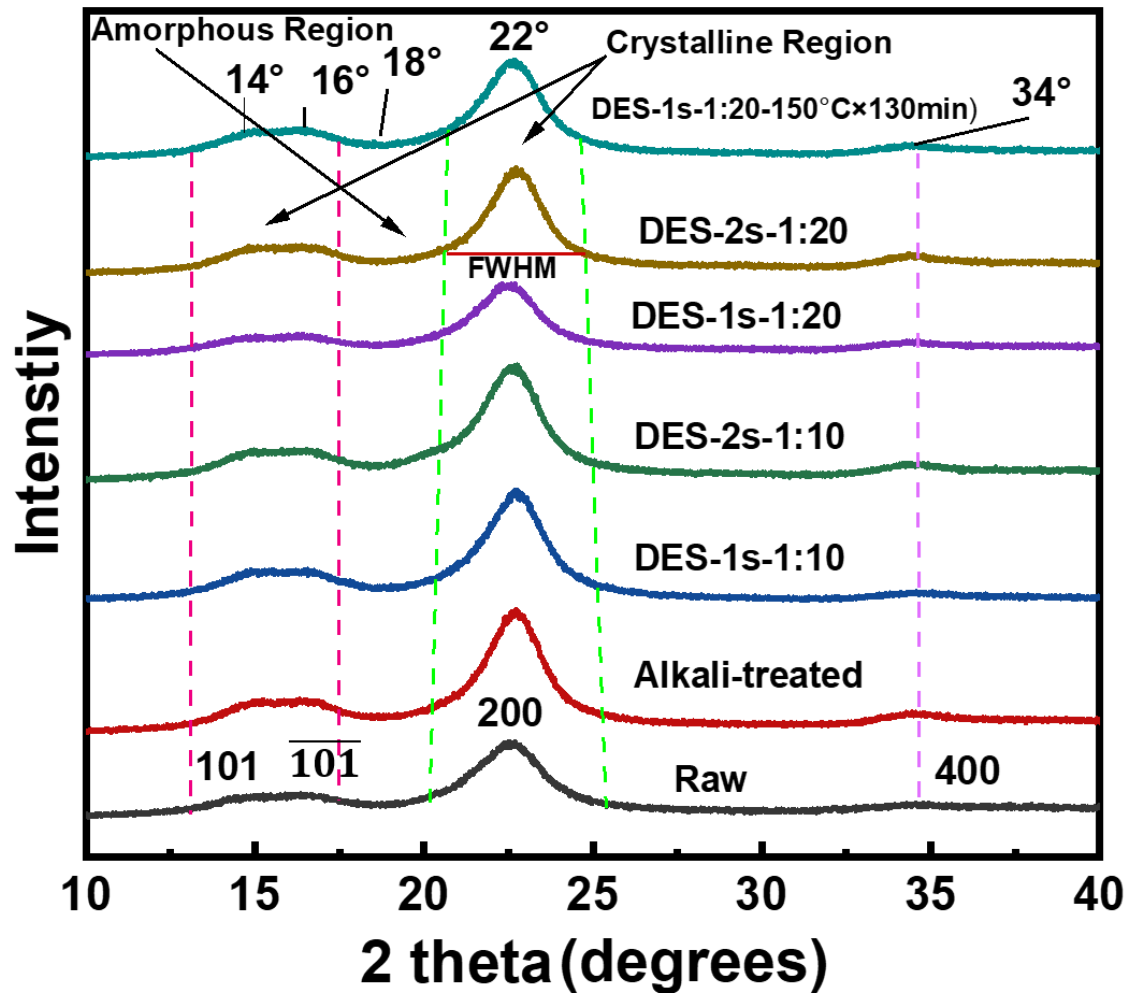


Figure 4.3. XRD spectra of raw and degummed hemp fibers

The crystalline profile of raw and degummed fibers was studied by X-ray diffraction. Figure 4.3 represents the XRD spectra of treated and untreated hemp fibers. The peaks at 14° and 16° were assigned to the characteristic peak of cellulose-I and appeared as a wide peak at raw hemp XRD spectrum due to the presence of lignin, pectin, and hemicellulose (Perel, 1990). The peaks at 14° ,

16°, 22°, and 34° corresponded to the crystalline phase of hemp fibers in planes 101, $\overline{101}$, 200, and 004, respectively (Hosseinmardi et al., 2018). The peaks of the crystalline phases were intensified and strengthened after alkali and DES treatment with the strongest peak for the DES treatment at 1:20 ratio. This indicates the impact of DES treatment on the orientation of crystalline cellulose. In a similar fashion, the intensity of amorphous region peak at 18° was decreased as was expected after the DES treatment at higher ratio and temperature.

The two peaks at 14° and 16° gradually became closer for the alkali-treated and DES treated samples (as the solid: liquor ratio and time-temperature of the degumming process increased), signifying the increased crystalline lattice and the removal of lignin, pectin, and hemicellulose. The crystallinity % and crystallite size of both degummed and undegummed hemp fibers were determined by using equation-2 and equation-3, respectively from XRD spectra (figure 4.3) and the results are summarized in table 4.2. The crystallinity % of the DES-treated fibers was increased as compared to that of raw hemp fiber. It was an obvious indication of the removal of non-cellulosic components (non-crystalline elements) from the hemp fiber structure.

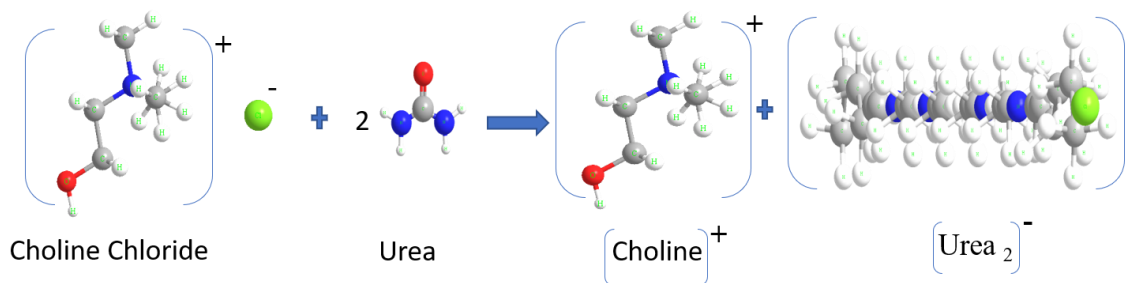


Figure 4.4. DES network (Ashworth et al., 2016)

It was an obvious indication of the removal of non-cellulosic components (non-crystalline elements) from the hemp fiber structure. Therefore, DES enables the cellulose chains to be tightened and strengthened, as referenced in the literature (Besbes et al., 2011). It was

reported from previous research that the removal of gummy materials facilitates the cellulose chains to be relaxed (increased stress relaxation) (Viscusi et al., 2020).

Table 4.2. Crystalline profile of treated and untreated hemp fibers

Samples	Crystallinity %	Crystallite size (Å°)	X_c	$FWHM$
Raw hemp	32.93	31.19	22.47962	2.71258
Alkali-treated	52.57	37.88	22.64723	2.23409
DES-1s-1:10	49.00	34.50	22.64892	2.4532
DES-2s-1:10	47.72	35.45	22.52912	2.38686
DES-1s-1:20	53.54	34.31	22.43262	2.46534
DES-2s-1:20	58.20	38.64	22.68784	2.19032
DES-1s-1:20 (150C*130min)	54.71	34.82	22.55745	2.43003

Therefore, microfibrils of the cellulosic components might get rearranged; the polymeric chain and surface morphology after alkali or DES treatment could be altered due to the reaction of Na^+ and hydroxyl groups of fibers (for alkali-treated), and cationic component (choline⁺) of DES network and hydroxyl groups of fibers (as can be seen in figure 4.2).

4.4. TG Analysis

Figures 4.5 and 4.6 represent the TGA curves and derivative TGA curves of treated and untreated hemp fibers. The heterogeneous chemical composition of natural fibers makes thermal degradation complex. (Poletto et al., 2015; Stevulova et al., 2017). The thermal degradation of hemp fibers can be divided into three thermal stages such as water evaporation at 50°C - 150°C, hemicellulose decomposition at 220°C - 300°C, and cellulose degradation at 300°C - 400°C (Yang et al., 2007). However, it is thought that the thermal degradation of lignin begins at roughly 280°C and ends at about 450°C. The complex aromatic nature of lignin enables lignin to keep thermal stability at a higher temperature; therefore, it can slow down the decomposition of

cellulose to some extent in terms of the thermal degradation event of cellulose (Fisher et al., 2002; Viscusi et al., 2021).

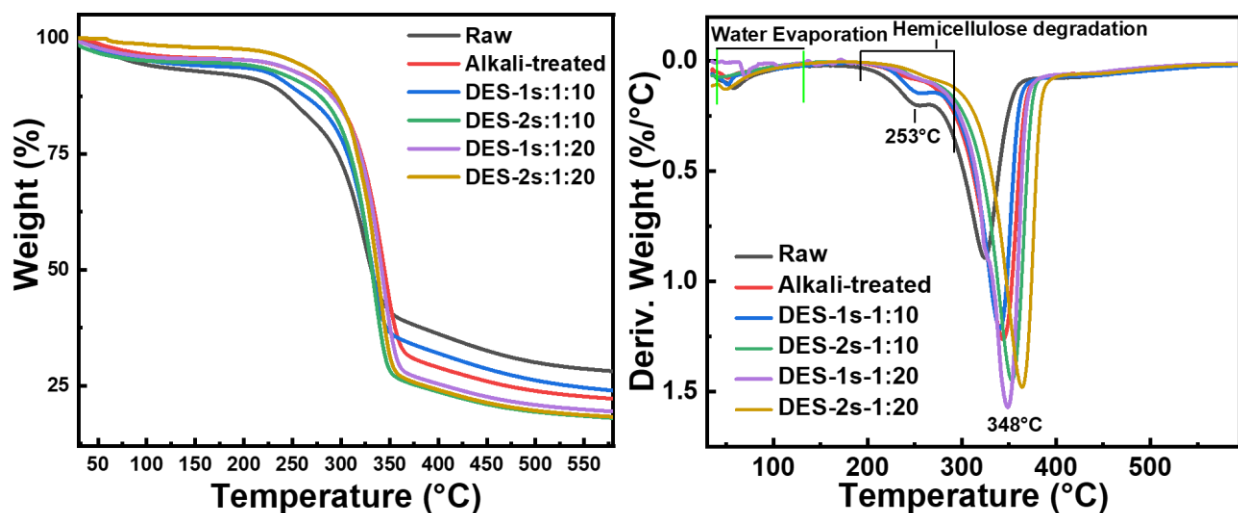


Figure 4.5. TG curve of degummed and undegummed hemp samples

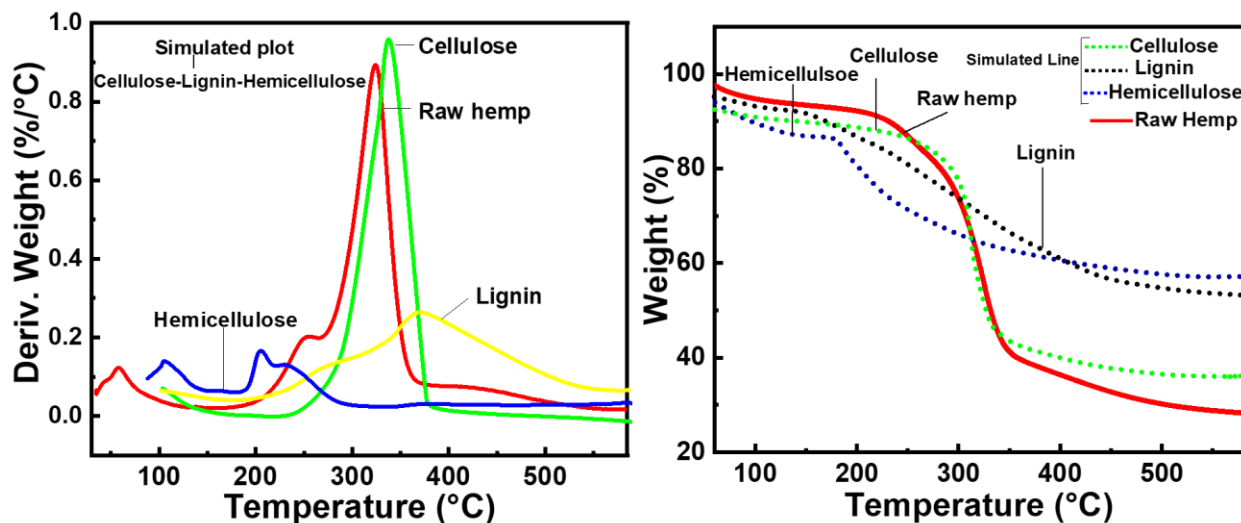


Figure 4.6. Derivative TGA curve of degummed and raw hemp fibers

Microwave-DES treated samples and alkali-treated samples both demonstrated a small amount of water evaporation as compared to the raw hemp sample because of the reduction of OH groups (Viscusi et al., 2020). It is evident from the TGA thermograms (figure 4.5 and 4.6) that hemicellulose has lower thermal stability as the degradation of hemicellulose observed at

Table 4.3. TGA profile of both treated and untreated hemp fibers

Sample	Onset Temperature (°C)	Peak Maximum at DTG plot (°C)	Char Content at 600°C (%)	Weight Loss at 600°C (%)
Raw	287	324	27.51	65.28
Alkali	311	344	21.87	77.28
DES-1s-1:10	310	340	23.39	74.62
DES-2s-1:10	316	348	17.78	82.22
DES-1s-1:20	322	353	21.12	78.88
DES-2s-1:20	318	349	19.89	80.11

Table 4.4. Weight Loss% and different thermal degradation stages of both degummed and undegummed hemp fibers

	1 st thermal degradation 50-150°C	2 nd thermal degradation 220-300°C	3 rd thermal degradation 300-400°C
Samples	Weight Loss%		
Raw hemp	5.246	17.21	36.65
Alkali-treated	3.106	9.698	55.83
DES-1s-1:10	4.129	11.22	48.37
DES-2s-1:10	2.842	8.500	60.23
DES-1s-1:20	2.875	7.497	60.17
DES-2s-1:20	1.811	8.256	63.00

256°C for raw hemp and DES-1s-1:10 sample (on the other side, the absence of the hemicellulose peak in DTG curve indicates the removal of hemicellulose from the DES-2s-1:10, DES-1s-1:20, and DES-2s-1:20 sample), which would facilitate the second stage thermal degradation (lignin thermal degradation) for a longer period (Viscusi et al., 2020) which might help lignin to have higher thermal stability. The Thermogravimetric profile of both degummed and undegummed hemp fibers is represented in tables 4.3 and 4.4.

At the third degradation stage, the peak at 300°C - 375°C represents the cellulose degradation, and 375°C - 400°C could be assigned to the oxidative degradation of cellulose

(Fisher et al., 2002). However, DES-treated fibers, especially the DES-2s-1:10, DES-1s-1:20, and DES-2s-1:20 had higher thermal stability (shifting the degradation peak toward higher temperature in TG curves for all the degummed samples) as the degradation starts from 320°C to 375°C. The main weight loss of raw hemp fibers was recorded at about 225°C - 390°C while the treated hemp fibers showed their main weight loss in the 250°C - 390°C region as can be seen in figure 4.5. The onset points of DES-treated hemp fibers including alkali treated fibers moved from 287°C to 310°C - 318°C, as similarly found by Fan et al. (2010) (figure 4.5). The thermal degradation of cellulosic components usually occurs at higher temperatures compared to that of non-cellulosic components (Fan et al., 2010). The increased onset temperatures in DES-treated fibers indicated the removal of the most non-cellulosic components from the fiber structure. The removal of non-cellulosic components helps cellulose to be rearranged in such a way to increase crystallinity with the densely packed rearrangement of glucose molecules, and it renders high thermal stability to cellulose since densely packed crystalline rearrangements slow down thermal decomposition.

4.5. Differential Scanning Calorimetry (DSC) Analysis

Linked water (OH groups) to cellulose and hemicellulose have higher thermal stability (Kabir et al., 2013), thus water evaporation occurred in the raw hemp in the range of 50°C - 150°C. On the other hand, the range in DES treated fibers was 50°C - 140°C. Water evaporation for the alkali treated fibers occurred at 50°C - 135°C (see figure 4.6). It can be assumed that there was therefore a reduction of hydroxyl groups in the DES-treated and alkali-treated samples. The removal of hemicellulose and improved hydrophobicity of the treated fibers results in a higher thermal stability for cellulosic compounds. According to TGA data (figure 4.5), after 350°C in the first heating run, more than 75% of the hemp samples is decomposed. However, in

the DSC figure 4.7, the main observation should be centered on the glass transition (T_g) of cellulose in the raw and DES treated samples. Glass transition of dry cellulose occurs at 200-250°C depending on its molecular weight, crystallinity, and structure (Kubát et al., 1967). T_g of 70% crystalline cellulose containing 2% water (playing the role of a plasticizer) drops to 160°C (Szcześniak et al., 2008). The T_g of the raw hemp sample is clearly observed right around 250°C, but this transition is absent in all other alkali and DES treated samples, obviously due to the plasticizing effect of some remnants after heating to 150°C (see table 4.4).

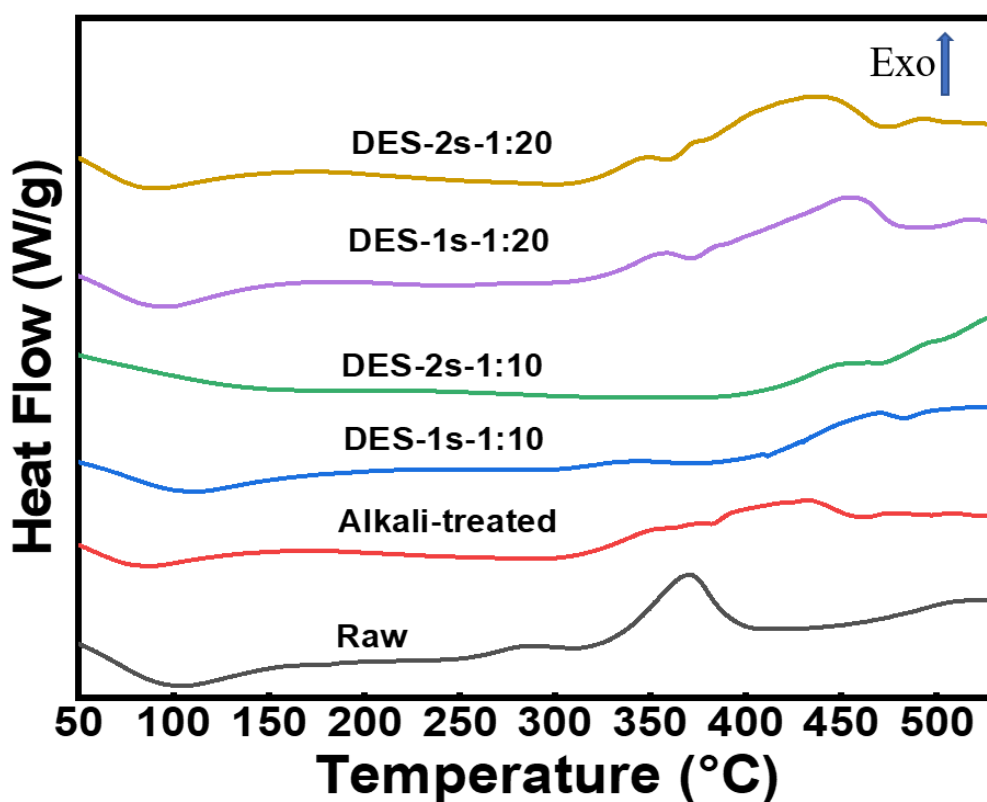


Figure 4.7. DSC spectra of both degummed and undegummed hemp fibers

Since below T_g , all materials become rigid, one may conclude that the rigidity of alkali and DES treated samples is practically absent and that these fibers might exhibit a certain degree of elasticity. In the DSC curve shown in figure 4.7, cellulose started to degrade 320°C - 400°C with the exothermic peak around 370°C for the raw hemp fiber. The exothermic peak for the DES-

treated fibers was shifted towards a higher temperature and DES-1s-1:20 demonstrated an exothermic peak around 450°C, which confirmed the higher thermal stability of the cellulose in the DES treated fibers.

Hemicellulose decomposition occurred between of 50°C - 320°C with an exothermic peak at 287°C for raw hemp fibers (Stevulova et al., 2017). The disappearance of this exothermic peak in the treated fibers validated the removal of hemicellulose. DES treated and alkali treated fibers showed a small endothermic peak at around 376°C - 390°C, thus, it can be concluded that the removal of hemicellulose resulted in a higher thermal stability of the treated fibers as the broad exothermic peak of cellulose in the raw hemp fibers at about 372°C moved toward 435°C for the alkali treated fibers, while DES treated fibers had a peak between 450°C - 473°C.

Lignin in natural fibers normally has the decomposition range between 250°C -450°C (Gargol et al., 2021; Stevulova et al., 2017; Tang et al., 2018), which is followed by the raw hemp fibers in this study. The aromatic structure of the lignin (aromatic hydrocarbons, hydroxy phenolics, guaiacyl, and syringyl compounds) enables lignin to have a broader range of degradation temperatures, which is supported by the DES-treated fibers and alkalized fibers. However, DES treated fibers and alkalized fibers showed degradation of lignin up to 520°C, indicating higher thermal stability of the treated fibers. In summary, it can be concluded that purification and less variation occurred with DES-treated hemp fibers, which resulted in a higher thermal stability of the fibers.

4.6. Solid-State NMR Analysis

CP-MAS/¹³C-NMR is an effective technique to illustrate the structure and chemical composition of polymeric materials (Otte et al., 2014). ¹³C NMR has been applied to both qualitative and quantitative studies of lignin since 1980 (Fu et al., 2015). The peaks in the

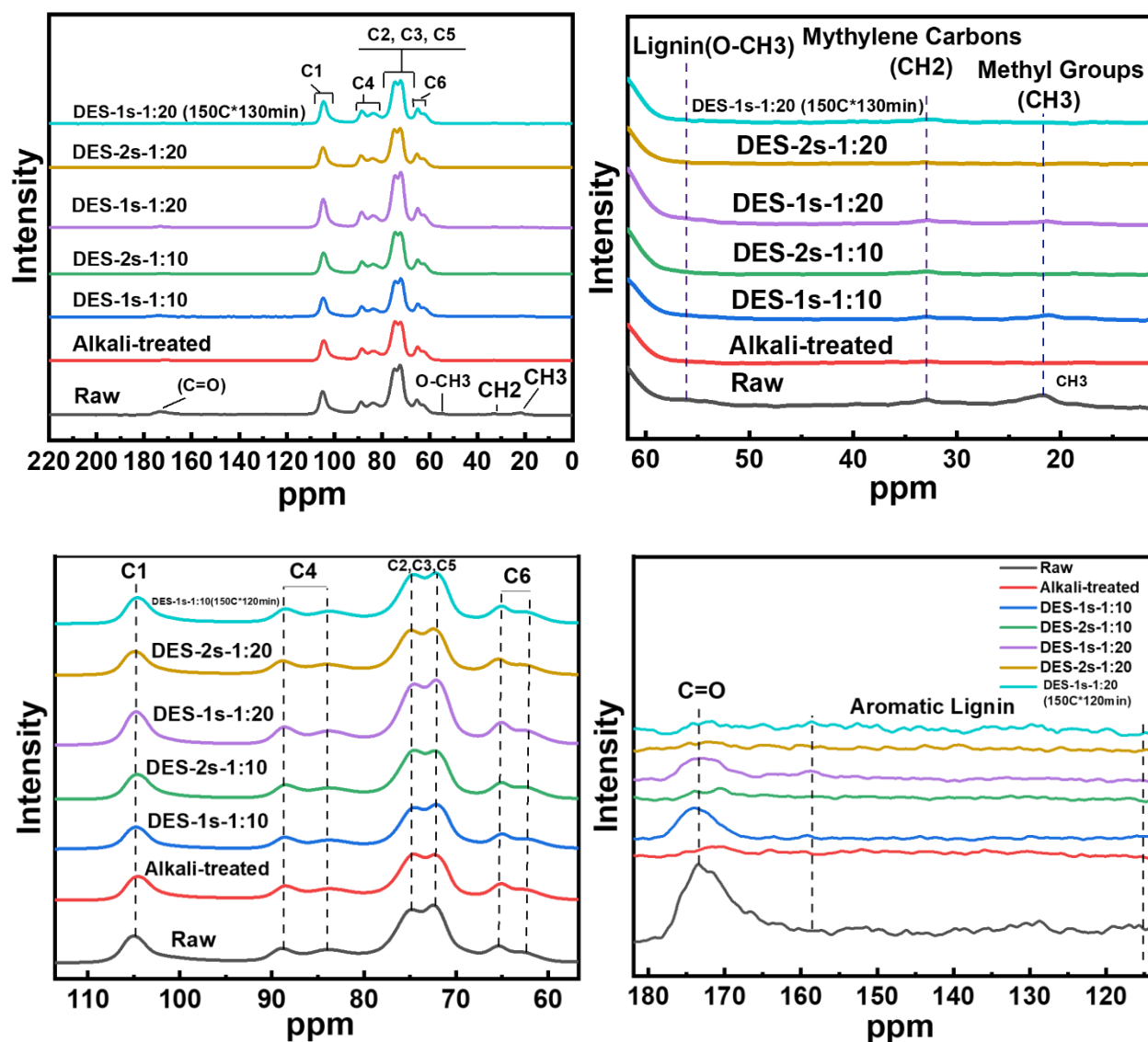


Figure 4.8. CP-MAS/ ^{13}C -NMR spectra of both treated and untreated hemp fibers

60-110 ppm (figure 4.8) range revealed the solid-state NMR spectra of cellulose and hemicellulose (Kang et al., 2019). The chemical shift at 105 ppm corresponds to the cellulose C1 carbons, and the up-field shoulder peak at 103 ppm is attributed to the hemicellulose or xylan carbons (Terrett et al., 2019). The C4 carbon of cellulose showed a peak in the spectra at 89 ppm, which is ascribed to the carbons of the crystalline region. However, the peak at 84 ppm comes from the amorphous region (Baccile et al., 2014). The broad peak from 72 ppm to 75 ppm corresponds to the cellulose carbons superimposed to the nearby xylan peaks. Carbon C6 of

crystalline and amorphous cellulose has a similar type of observations and interpretations at 63 ppm to 65 ppm by Bonatti et al. (2004). Carbonyl and methoxy groups of lignin showed peaks at 174 ppm and 56 ppm, respectively (Moussa et al., 2020). As shown in figure 4. 8, raw hemp fiber had a broad peak at 174 ppm, and 56 ppm that gradually became absent in the Microwave-DES treated fibers (as the temperature, time, and solid-liquor ratio increased) and alkali-treated fibers. It was a clear indication of the removal of lignin and breakage of hemicellulose to be turned into glucose molecules and contributed to increased crystallinity and chemical composition rate of cellulose in the fiber structure. This phenomenon has a closer agreement with the XRD spectra of the raw and degummed hemp fibers.

In addition, the broad peak at 21 ppm and the small peak at 32 ppm in the raw hemp are assigned to the methyl groups and methylene carbons of lignin and xylan, respectively. However, after DES treatment, those peaks were nowhere to be found (as can be seen in figure 4.8) (Nishida et al., 2017).

The disappearance of the peaks is indicative of the removal of gummy compounds in the treated fibers. Lignin, a complex biopolymer can be derived from the polymerization of phenyl propane monomers, synapsyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol (Grabber et al., 1997; Hansen et al., 2016). These carbons of monolingol units exist in the aromatic lignin region as amino acid groups in the raw hemp fibers, disappearing after the alkali and DES treatment (figure 4.7). The signals in the NMR spectra of raw hemp fibers at 21 ppm and 174 ppm are the consequence of agglomeration and interaction of hemicellulose and methyl moieties associated with acetyl groups (Foston et al., 2012; Simmons et al., 2016; Teleman et al., 2001). The signal at 81 ppm of carbon-4 is also generated due to the interaction of cellulose and xylan present in the raw hemp fibers (Foston et al., 2012). This wide-ranging signal disappeared after DES and

alkali treatment. This is caused by the removal of hemicellulose and lignin from the fiber structure, which is also supported by the previous literature (Hosseinmardi et al., 2018). It is possible to find the carbon ratios which existed in the lignin structure by an integration of the area between 110 ppm-160 ppm (Fu et al., 2015). According to the literature, the chemical shift at 64 ppm could be assigned to the carbon-5 of xylan or hemicellulose (Simmons et al., 2016), and this signal was flattened after DES and alkali treatment, indicating the removal of hemicellulose.

Table 4.5. Chemical compositions of both degummed and undegummed fibers

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Others (%)
Raw	58.40	21.30	18.57	1.73
Alkali-treated	87.3	7.05	5.65	-
DES-1s-1:10	84.58	6.93	8.49	-
DES-2s-1:10	86.06	6.97	6.97	-
DES-1s-1:20	87.57	6.27	6.16	-
DES-1s-1:20	86.83	7.12	6.05	-

A similar explanation can be used for the NMR band at 84 ppm. Therefore, the integration of the area under those two peaks (64 ppm and 84 ppm) can be an estimation of hemicellulose content in the fiber structure. Table 4.4 represents an estimation of the chemical composition of hemp fibers obtained from Solid-state NMR spectra using the Gaussian - Lorentzian Model and peak deconvolution.

4.7. UV-Vis Analysis and UV Shielding Property

The UV shielding performance of both treated and untreated hemp fibers were analyzed according to AS /NZS 43 99, Appendix A standard as a schematic of UV shielding of fiber films shown in figure 4.9. It is evident that all the hemp samples had excellent UV protection properties (all the hemp fiber samples have the transmittance % at a range of 0% - 0.06%) (see

figure 4.10). Among all the hemp samples, DES-2s-1:10 sample had the lowest UPF value, even though other DES treated samples also had excellent UPF values (as shown in table 4.5).

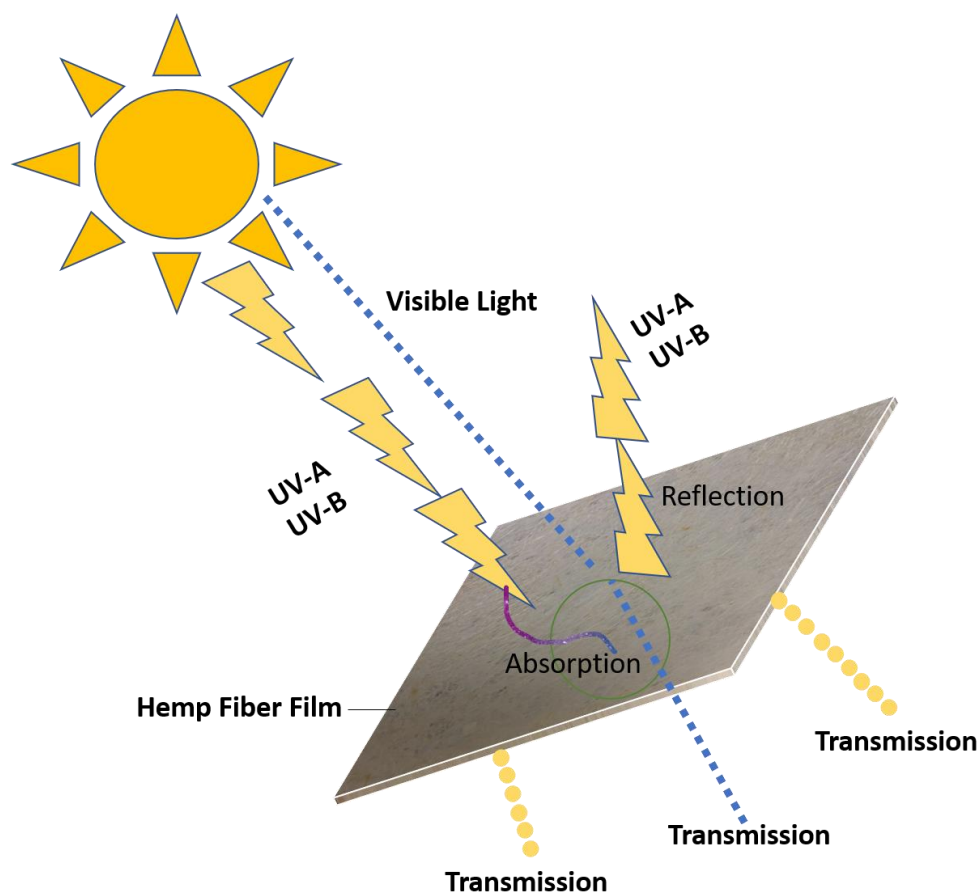


Figure 4.9. A schematic of UV-shielding of hemp fiber films

It is obvious that there is a tendency to have a lower value of UPF after treating with NaOH since aggressive alkali treatment removes most of the lignin content from the fiber surface. The aromatic structure of lignin aids to block the UV radiation in the raw hemp fibers. The phenolic hydroxyl, carboxyl, and carbonyl groups in the lignin structure are responsible for generating heat when the fiber is subjected to photon energy of UV light (Y. Zhang et al., 2020). However, these phenolic groups, especially hydroxyl groups in the lignin could absorb the generated heat and also are able to quench the active radicals through the mechanics of electron transfer (Dean et al., 2013).

Table 4.6. UPF value of treated and untreated hemp fiber

Sample	UPF
Raw	140.75
Alkali-treated	127.47
DES-1s-1:10	118.11
DES-2s-1:10	102.43
DES-1s-1:20	183.67
DES-2s-1:20	118.55

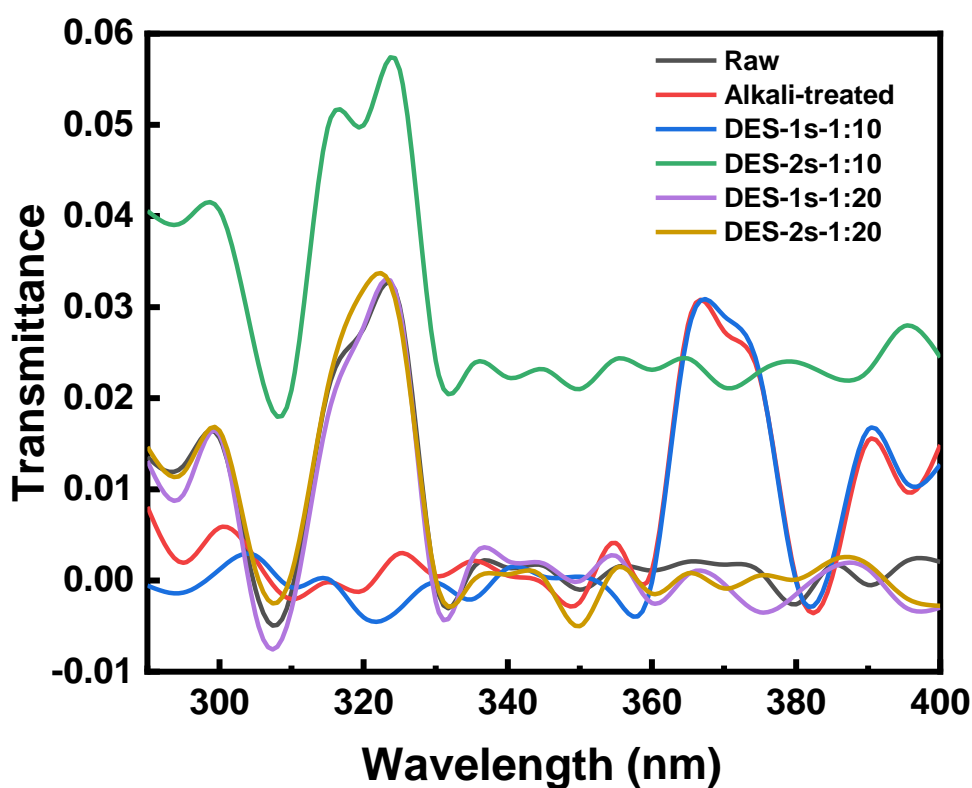


Figure 4.10. UV-vis spectra of both degummed and undegummed hemp fibers

The presence of the lignin in the fiber structure facilitates improved UV blocking performance. For instance, DES-1s-1:10 had a UPF value of about 118 and after NaOH treatment referred to as DES-2s-1:10 in this study, the UPF value was reduced to 102.43. A similar trend was observed for the DES-2s-1:20 sample (table 4.5).

However, DES treated samples have similar kind of UV protection for the DES treated sample at 1:10 and higher concentration of Fiber: DES solvent (1:20) provides increased UPF values (e.g, DES-1s-1:20 has the UPF value of 183). There is little published studies about the contribution of DES solvent in the degummed lignocellulosic materials in terms of UV protection. However, DES made of glycerol and choline chloride with alpha hydroxylate anions exhibited crosslinking and plasticizing ability in the polysaccharide matrix (Zdanowicz et a., 2019). The improved UV blocking performance of DES treated samples could thus be explained by the involvement of DES solvent in the fiber structure. This phenomenon probably happens due to the interference of the DES solvent as a crosslinking and plasticizing agent when it comes contact with the fiber structure. In addition, the presence of a low lignin content in the degummed fibers accelerated the UV shielding performance in the DES-treated fibers.

CHAPTER 5. CONCLUSION AND FUTURE RESEARCH RECOMMENDATION

Degumming or surface modification of hemp fibers is crucial for further fiber processing with respect to textile applications or composite manufacturing. A novel method was developed to degum the hemp bast in our study by utilizing DES and microwave energy. Results revealed that DES treatment of hemp fibers were comparable with the traditional alkali treatment in terms of increased cellulose content in the degummed fibers. Furthermore, DES was able to extract hemicellulose and lignin effectively which was validated by FT-IR and NMR. In the same fashion, DES treated fibers demonstrated a clean surface which was confirmed by SEM analysis. Consequently, DES treated fibers showed higher thermal stability and increased crystallinity. Therefore, DES treatment can be a novel path for degumming of natural fibers, including hemp fibers, for the purpose of improving fiber qualities in all distinct aspects of sustainable subsequent fiber processing. However, future research can be conducted on the reusability and recovery of DES-waste liquid.

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